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RACEMIZATION AND SOLVOLYSIS OF  
SULFONIUM IONS



BY

GUY TOURIGNY

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA      SEPTEMBER 1967



THE UNIVERSITY OF ALBERTA  
FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled "Racemization and Solvolysis of Sulfonium Ions" submitted by Guy Tourigny, B.A., B.Sc., in partial fulfillment of the requirements for the degree of Doctor of Philosophy.



To  
Evelyn





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## ABSTRACT

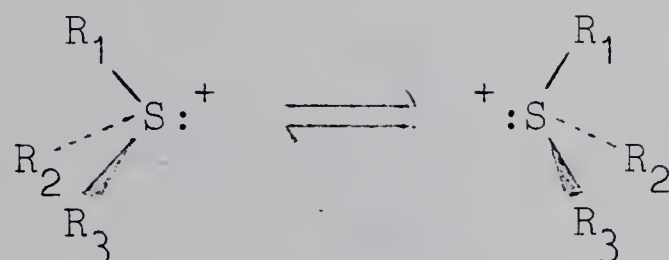
The racemization and solvolysis of t-butylethylmethylsulfonium perchlorate (I) were investigated.

Optically active I was obtained by resolution of the corresponding (-)-dibenzoylhydrogentartrate followed by replacement of the anion by perchlorate. Compound I racemizes faster than it solvolyzes in a variety of solvents. The results will be discussed with reference to the effects of varying the anion, ionic strength, solvent and temperature. There are two mechanisms which would account for racemization. (i) A heterolytic carbon-sulfur bond cleavage to yield a t-butyl cation-ethyl methyl sulfide ion-neutral molecule pair which could return to racemic sulfonium salt or react with solvent to form products, and (ii) inversion about the central sulfur atom analogous to the inversion of an ammonia molecule.

A distinction between the two mechanisms can be made on the basis of the effect of substituents on the reaction. 1-Methoxy-2-methyl-2-propylethylmethylsulfonium (ii), t-amylethylmethylsulfonium (III) and 1-phenyl-2-methyl-2-propylethylmethylsulfonium perchlorates (IV) were prepared and resolved. The relative rates of ethanolysis at 50° of compounds I : II : III : IV are 1 : 0.06 : 6.3 : 1.1. These relative rates show the decrease and increase expected for a heterolytic cleavage



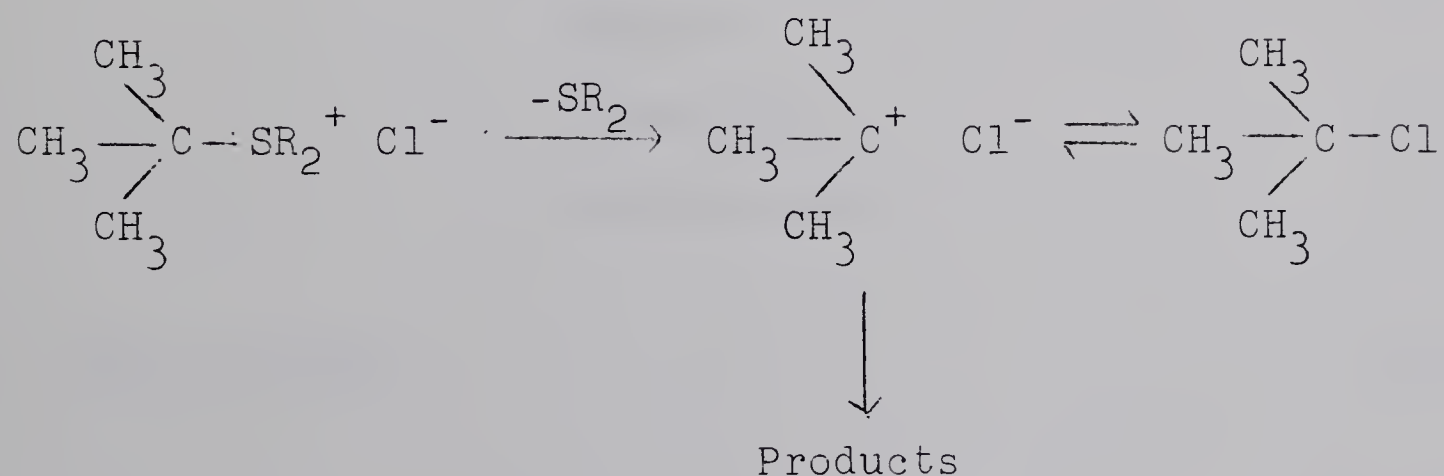
in which electron-withdrawing and electron-donating groups are introduced as substituents on the t-butyl group. In contrast, the relative rates of racemization in ethanol at 50° of compounds I : II : III : IV are 1 : 1.7 : 3.8 : 4.7. The replacement of a hydrogen of the t-butyl group by a substituent accelerates the rate of racemization whether the substituent is electron-withdrawing or electron-donating. This effect cannot be electronic in origin and instead must be associated with an increase in the non-bonded interactions in the ground state relative to the transition state for racemization on introduction of the substituents. The results indicate that racemization of t-butylethylmethylsulfonium salt involves a pyramidal inversion.



The product distribution obtained from the solvolysis of sulfonium salts is strongly influenced by the anion present in the solution. The fraction of elimination for ethanolysis of t-butylethylmethylsulfonium bromide is greater than that for t-butylethylmethylsulfonium perchlorate but similar to that for t-butyl bromide.



Changing the solvent from ethanol to acetic acid caused a small decrease in the fraction of elimination for the sulfonium perchlorate but caused a large increase in the fraction of elimination for the sulfonium bromide and t-butyl bromide. Addition of lithium chloride or acetate also produced a marked effect on the product distribution whereas the addition of lithium perchlorate had no effect. The formation of t-butyl chloride was observed during ethanolysis and acetolysis of t-butylethylmethylsulfonium perchlorate in the presence of lithium chloride. The results are explained in terms of a common ionic intermediate for the solvolysis of sulfonium halides and their corresponding alkyl halides. This intermediate may be a t-butyl cation halide ion ion-pair.







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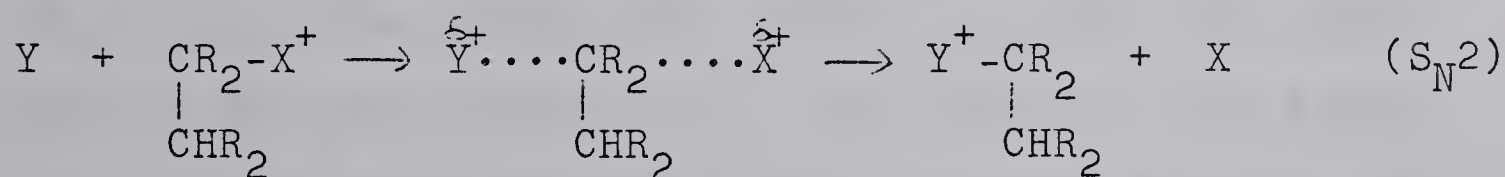
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## INTRODUCTION

Solvolysis reactions are among the most intensively studied reactions in organic chemistry. The investigation of stereochemistry as well as solvent, salt, substituent and isotope effects on kinetics and product distribution has contributed greatly to the understanding of the mechanism of reactions in solution.

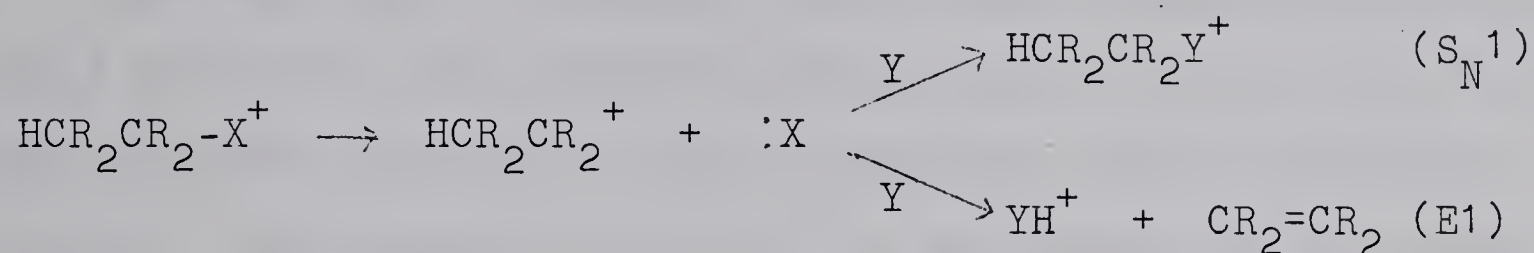
Ingold and co-workers (1) over a period of years postulated and developed two mechanisms for nucleophilic substitution reactions in solution. The "bimolecular" mechanism ( $S_N2$ ) involves only one stage and can be envisioned as the synchronous approach of the nucleophile and decomposition of the substrate. The mechanism may be formulated as shown below although three other charge types exist since Y may be negatively charged or neutral and X may formally be neutral or positively charged.



The unimolecular mechanism ( $S_N1$ ) was formulated as two steps as shown below. The first step involves the breaking of the C-X bond to form a carbonium ion and the second step involves the reaction of the carbonium ion with any available nucleophile, frequently a solvent molecule, to form products. In



addition, if the carbonium ion possesses a  $\beta$ -hydrogen, loss of a proton can occur resulting in the formation of an olefin. This reaction was labeled E1. In unimolecular reactions, the rate is determined by the common slow stage, ie. ionization, but the product ratio is determined by competition between succeeding fast stages.



At first this proposal met considerable opposition, however as the importance of ionic solvation was realized, the  $\text{S}_{\text{N}}^1$  and E1 hypotheses have been generally accepted as a major step in the development of theoretical organic chemistry.

A necessary consequence of the unimolecular hypotheses is that the ratio of elimination to substitution must be independent of the leaving group, whether  $\text{-Cl}$ ,  $\text{-Br}$ ,  $\text{-I}$ ,  $\text{-SR}_2^+$ ,  $\text{-NR}_3^+$ , etc., even though the specific rate for the total reaction may vary greatly (2). The concept of the planar carbonium ion surrounded by a solvent sheath requires that any optical activity due to asymmetry at the reaction center must vanish during solvolysis. However in many cases racemization is accompanied by varying amounts of net inversion. Hammett (3) suggested that the product of the ionization step is an ion pair and that a distinction should be made





between ionization and dissociation. Attack by the solvent on the ion pair may lead to inverted products whereas attack occurring after dissociation of the ion pair leads to racemic products. For a more complete discussion on the mechanisms of nucleophilic reactions, the reader should refer to the excellent reviews in the literature (1, 4-7).

The solvolysis of t-butyl- and t-amylethylmethylsulfonium salts was first investigated by Ingold and co-workers (2, 8-11). These systems represent a type of reaction (type 4 according to their classification) wherein the unit charge of the ground state undergoes dispersal in the transition state. The study was undertaken to confirm their theory concerning solvent effects on nucleophilic substitution and elimination (9, 12). Generally the theory considers solvation as an electrostatic phenomenon. Hence, a change to a more polar solvent will decrease or increase the energy of activation as the transition state becomes respectively more or less polar than the initial state of the reactants.

Applying these concepts to the solvolysis of t-butyl- and t-amyl-dimethylsulfonium salts, Ingold and co-workers predicted a small decrease in the rate of solvolysis and also a small decrease in the fraction of olefin produced as the ionizing power of the medium is increased. This was confirmed by their results. The rates of solvolysis of t-butyldimethylsulfonium iodide at 50° were  $1.78 \times 10^{-5}$ ,  $1.24 \times 10^{-5}$ , and  $0.60 \times 10^{-5} \text{ sec.}^{-1}$  in ethanol, 80% ethanol-water and water respectively. Varying the solvent from ethanol to 80% ethanol-





water decreased the rate of solvolysis of t-amyldimethylsulfonium iodide at 50° from  $15.5 \times 10^{-5}$  to  $6.66 \times 10^{-5}$  sec.<sup>-1</sup> and decreased the proportion of elimination from 64.4 to 47.8 per cent (8-11).

Saunders and co-workers (13, 14) have shown that the rate of solvolysis of t-butyldimethylsulfonium chloride has a rather large sulfur isotope effect. They found  $k_{32}/k_{34}$  equal to 1.018 in water and 1.010 in ethanol at 40°, suggesting that the carbon-sulfur bond is broken in the transition state.

Swain, Kaiser and Knee (15) established that the hydrolysis of t-butyldimethylsulfonium chloride is not significantly faster than that of the perchlorate in 90% acetone-water at 50° and concluded that the mechanism is not a slow reaction with anion followed by fast solvolysis. They also showed that the observed rates of solvolysis could not be correlated to various solvent parameters.

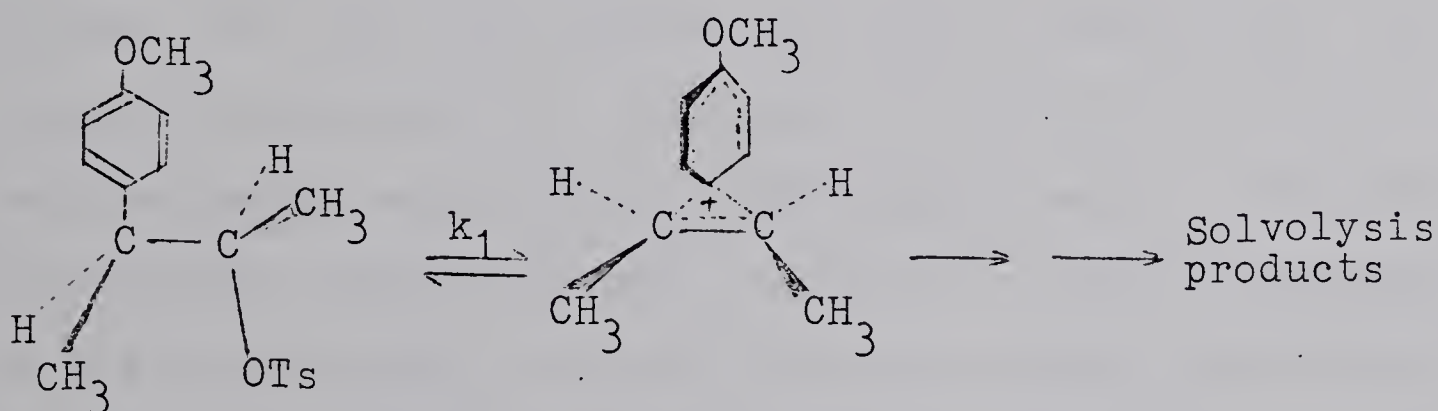
Hyne and his associates have published a series of papers on the solvolysis of sulfonium salts (16-22). They have studied the effects of concentration, anion type, solvent variation, added salts and alkyl group variation on the rates of solvolysis of sulfonium salts. The results were interpreted in terms of an increasing importance of an ion-pair mechanism as the composition of the medium is changed.

Cocivera and Winstein (23) have re-examined the products of solvolysis of t-butyl chloride, bromide, iodide and di-



methylsulfonium perchlorate in a variety of solvents. They observed that the fraction of elimination varies considerably with changes in solvent or leaving group.

Winstein and co-workers have developed methods for determining many of the intimate details of solvolysis reactions. One of the most powerful tools developed was the evaluation of ionization rate constants independent of solvolysis rate constants. For example, Winstein and Robinson (24) have shown that the racemization of optically active threo-3-p-anisyl-2-butyl p-bromobenzenesulfonate in acetic acid at 25° was four times faster than its solvolysis. Since anchimerically assisted ionization results in the formation of a symmetrical intermediate, loss of optical activity is a measure of total formation of the ion pair



independent of internal return. They proposed that the rate of racemization can be equated to the rate of ionization,  $k_1$ .

The evaluation of  $k_1$  by polarimetric studies is applicable only to systems which produce totally symmetrical

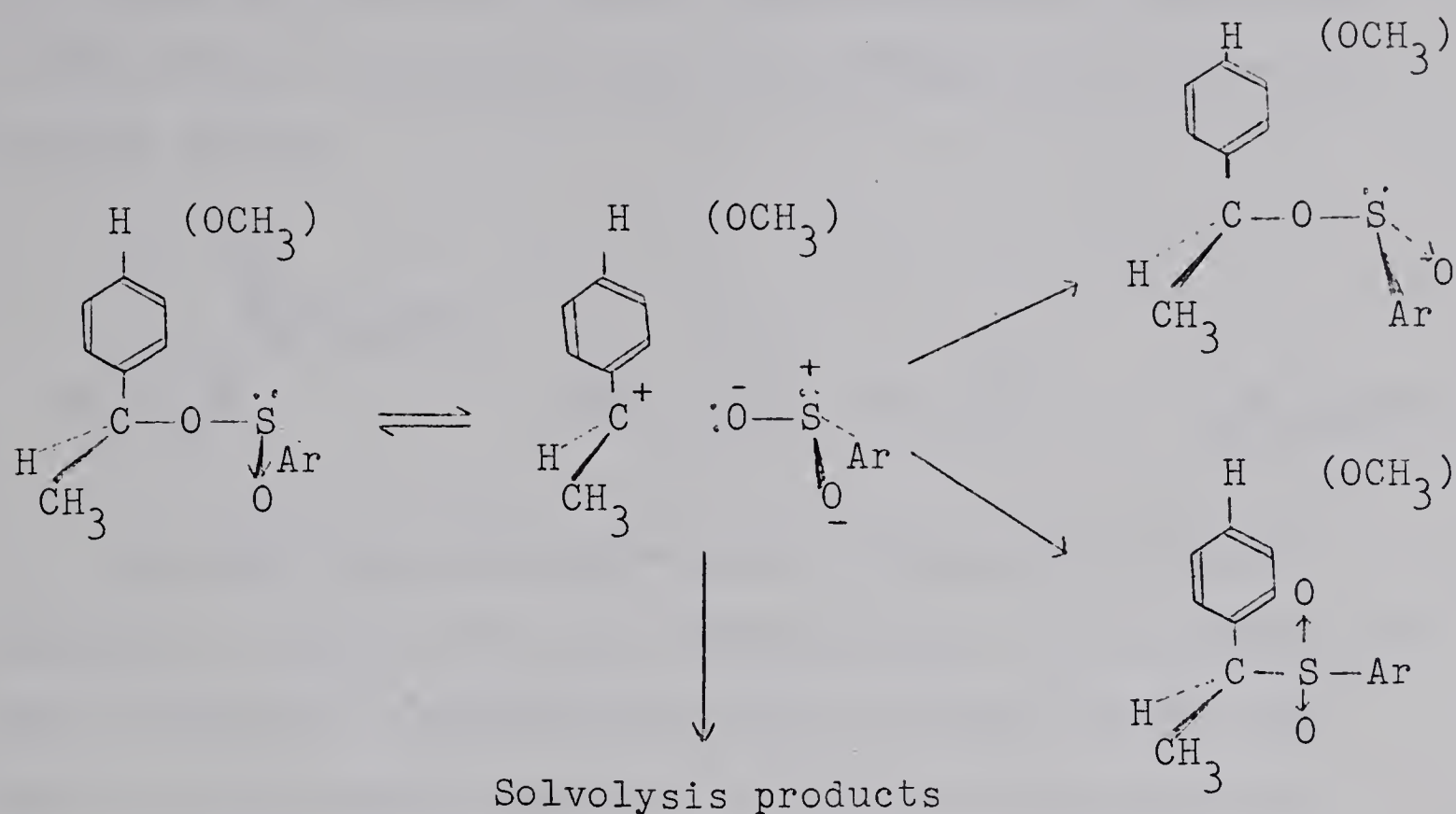


intermediates. In other systems, the rate of racemization is not necessarily equal to the rate of formation of ion-pairs because frequently the ion-pair is itself optically active and hence ionization may be faster than racemization. An unknown fraction of the ion-pair intermediate may revert to starting material with retention of configuration and consequently a portion of the return may not be detected. The rates of racemization of p-chlorobenzhydryl and  $\Delta$ -mesityl-ethylchlorides are greater than their rates of isotopic exchange and solvolysis (25, 26). In these cases the polarimetric rate represents only a lower limit to the rate of ionization.

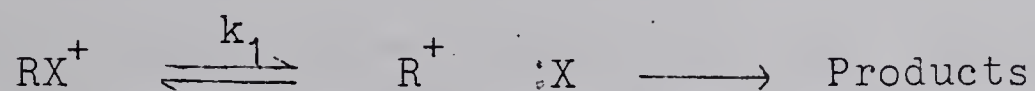
An alternative approach to the detection of ion-pair return in solvolysis is to attempt to observe the racemization of an optically active leaving group. Darwish and McLaren (27, 28) have demonstrated that  $\Delta$ -phenylethyl 2,6-dimethylbenzenesulfinate undergoes diastereomer interconversion during solvolysis in 60% ethanol-water. The rates of diastereomer interconversion, solvolysis and rearrangement to the corresponding sulfone all show similar sensitivity to the introduction of a p-methoxy substituent. A rate acceleration of over four powers of ten is observed for each reaction. This isomerization represents the first example of ion-pair return being detected, at least formally, by the racemization of the leaving group.







In principle, any system possessing an optically active leaving group that becomes inactive on ionization can be utilized to detect ion-pair return. Among the systems which meet this requirement are tertiary sulfonium and quaternary ammonium salts. Thus with the onium salts there arises the possibility of detecting ion-neutral molecule-pairs.

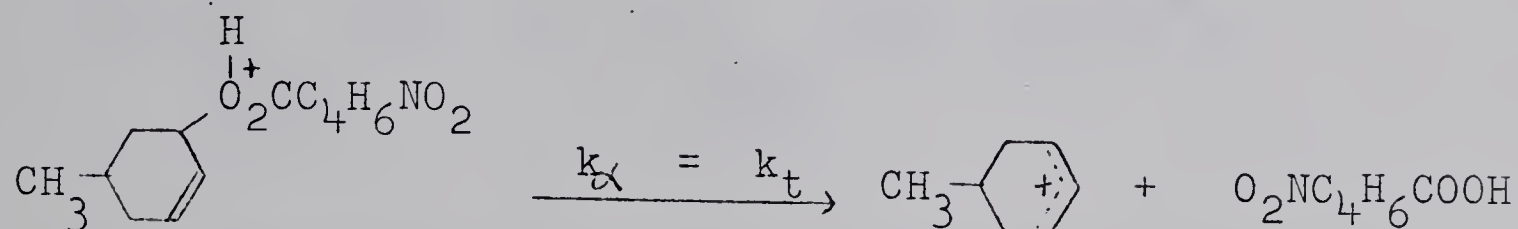


Goering and Silversmith (29, 30) have shown that ion-neutral molecule-pair return does not occur in the acid-catalyzed hydrolysis of 5-methyl-2-cyclohexyl p-nitrobenzoate in aqueous acetone. The conjugate acid of the ester undergoes heterolysis to give carbonium ions and p-nitrobenzoic

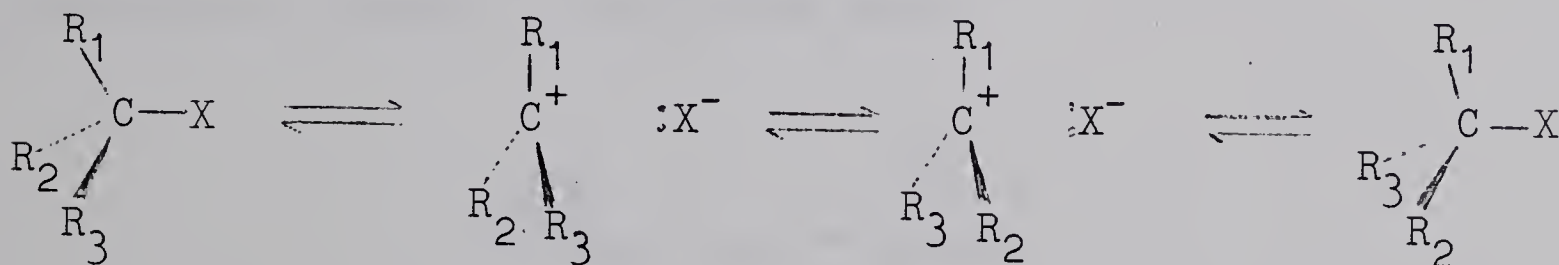




acid as shown below, but since the polarimetric rate is equal to the rate of solvolysis,  $k_{\alpha} = k_t$ , there is no detectable ion-pair return.



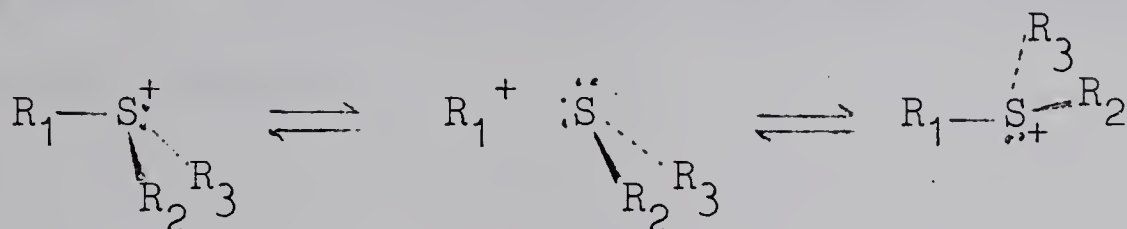
For open chain carbonium ions, racemization without solvolysis requires not only separation of the two groups and their subsequent recombination but also that the two ions must be sufficiently separated to allow rotation of one relative to the other as illustrated below.



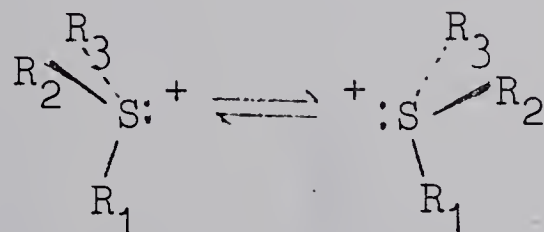
The racemization of an optically active sulfonium ion may be energetically much more favorable. Racemization would require bond heterolysis as the initial step. The recombination process which yields racemic salt will depend upon the hybridization of the sulfide sulfur. If  $sp^3$ , racemization is accomplished by recombination with the other electron pair; if  $p^3$ , racemization is accomplished by recombination with the other lobe of the p orbital. In either case a simple partial rotation with no further charge separation is



required. Hence, sulfonium salt solvolysis may be an effective tool to detect ion-neutral molecule-pairs.



Racemization of sulfonium salts could also, in theory, occur by a non-ionic pathway, ie. a pyramidal inversion mechanism analogous to that of the ammonia molecule. Mislow and co-workers (31) have shown that some alkyl sulfoxides undergo thermal racemization by an inversion process, but at the outset of this work there was no evidence for the inversion of sulfur in sulfonium salts.



The potential barrier restricting inversion in the ammonia molecule has been determined using data on the hyperfine splitting of certain lines in the infrared and microwave spectra (32). This method could not be applied to the sulfonium salt since no corresponding data are available in the literature. One can assume that a pyramidal model can be inverted by gradually increasing the amplitude of the symmetrical deformation vibrations as shown in



Figure I. The force constants controlling this vibration can be used to plot a double parabolic potential of the form  $V = A (\Delta\alpha)^2$  on either side of the planar configuration. as shown in Figure II.

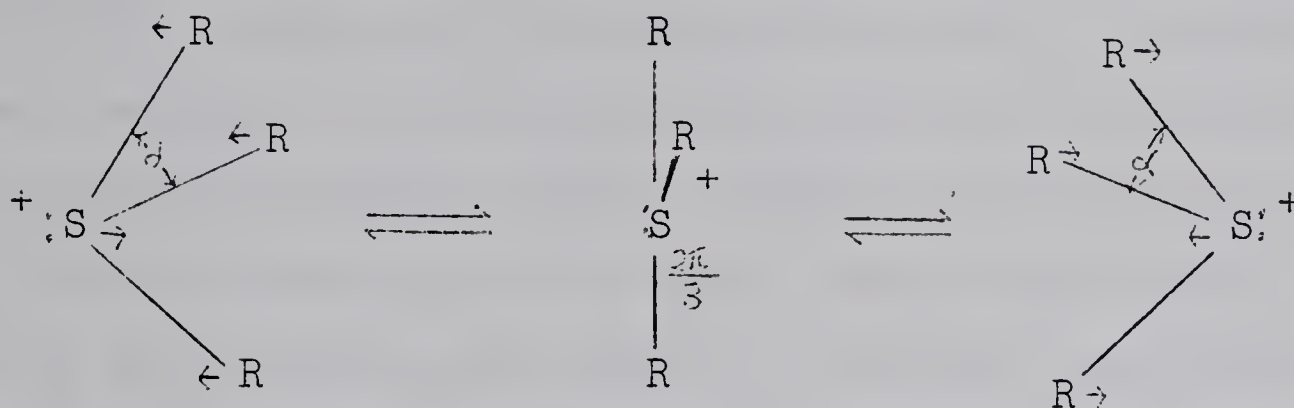


Figure I. Diagrammatic representation of inversion of  $\text{SR}_3^+$  by gradually increasing the amplitude of the symmetrical deformation vibrations.

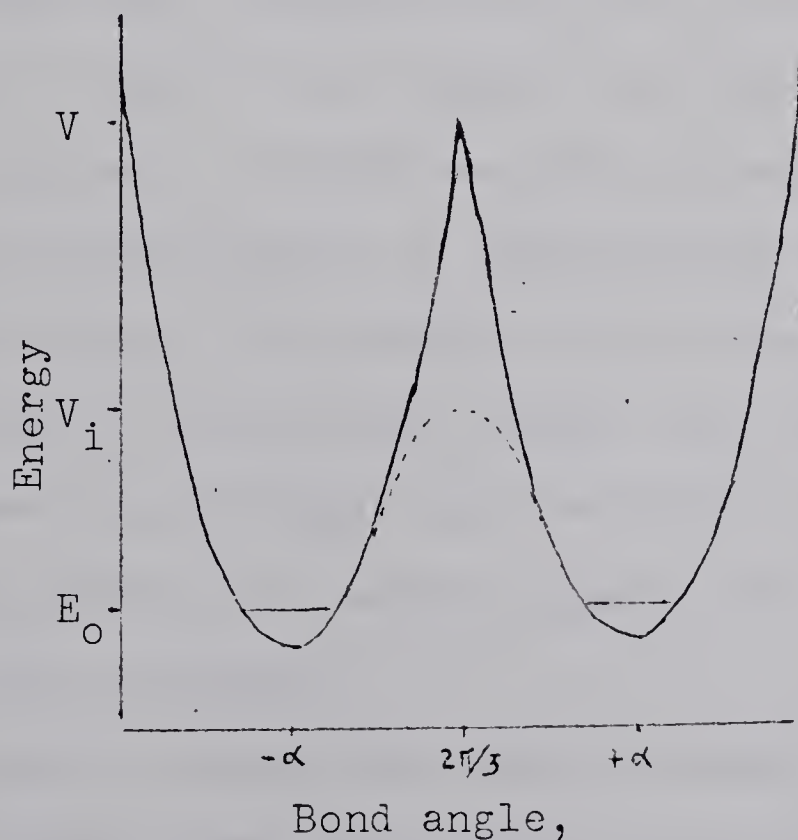


Figure II. Potential energy,  $V$ , for the inversion of the pyramid  $\text{SR}_3^+$  vs bond angle,  $\alpha$ . The solid line represents the parabolic function of Kincaid and Henriques (33), the broken line represents the valence force field function of Weston (34).





Kincaid and Henriques (33) used the parabolic potential function suggested by Wall and Glucker (35),

$$V = \frac{1}{2}k ( |x| - |x_0| )^2,$$

where  $x$  is the distance of S from the plane of R groups,  $x_0$ , the distance at equilibrium;  $k$  is the force constant,  $k = 4\pi^2\nu_3^2\mu$ , where  $\mu$  is the reduced mass and  $\nu_3$  the vibrational frequency. For trimethylsulfonium ion the authors used the following estimated values: 1.82Å for the C-S bond length, 109.5° for the bond angle (an upper limit, lower values will make the activation energy higher), 0.61Å for the equilibrium height, 600 cm.<sup>-1</sup> for the frequency (a lower limit, dimethyl sulfide has 648 cm.<sup>-1</sup>, higher values increase the calculated energy). They obtained a value of 100 kcal./mole for the activation energy required for intramolecular inversion. This value is so high that "flipping" of the trimethylsulfonium ion analogous to that of the ammonia molecule, would be an unobservable process. Kincaid and Henriques pointed out that the parabolic function tends to overestimate the value for the inversion energy. For example, the method gives a value for ammonia that is 50 per cent higher than the accepted value. However even a 50 per cent reduction in the value for the trimethylsulfonium ion would suggest that its inversion would be too slow to detect.

A more recent estimate was made by Weston (34). He applied the valence force field function proposed by Costain and Sutherland (36) to the double minima problem,





$$V(\alpha) = 3/2 \{ k_1 (\Delta l)^2 + k_\alpha (\Delta \alpha)^2 \}$$

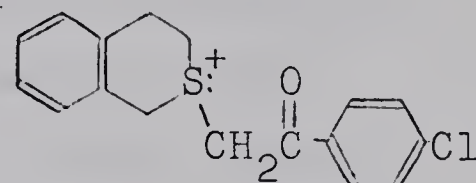
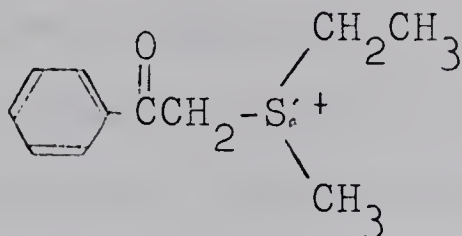
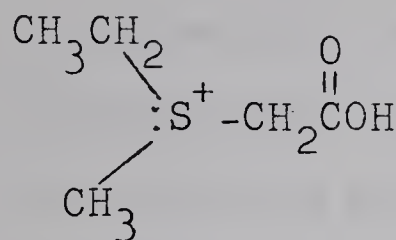
where  $k_1$  is the S-C bond stretching force constant,  $k_\alpha$  is the bond bending force constant,  $\Delta l$  and  $\Delta \alpha$  are the changes in bond length and bond angle from the equilibrium value. From symmetry coordinates involving  $\nu_1$  and  $\nu_2$  they could relate  $\Delta l$  to  $\Delta \alpha$  and thus obtain

$$V_i = K [(2\pi/3) - \alpha]^2.$$

Assuming the following values, 1.82Å for the bond length, 654 and 285 cm.<sup>-1</sup> for the vibrational frequencies, 109.5° for the bond angle, Weston obtained an activation energy of 16.5 kcal./mole; assuming a bond angle of 100° by analogy to trimethylphosphine gave 24.1 kcal./mole. The author pointed out that the values obtained are surprizingly low and suggested that this may be due to using force constants that are not corrected for vibrational anharmonicity.

The values obtained by Weston were known to be too low because optically active sulfonium salts are stable and have been known for a long time. In 1900, Pope and Peachey (37) resolved carboxymethylethylmethylsulfonium d-camphorsulfonate by recrystallizing the material 50 times. Addition of platonic chloride resulted in precipitation of the corresponding salt (m.p. 177°-180°, decomp.,  $[M]_D +30.5$ ). In the same year, Smiles (38) obtained the two optical isomers of phenacyl-ethylmethylsulfonium picrate by resolution of the d-bromocamphorsulfonate followed by the addition of picric acid.

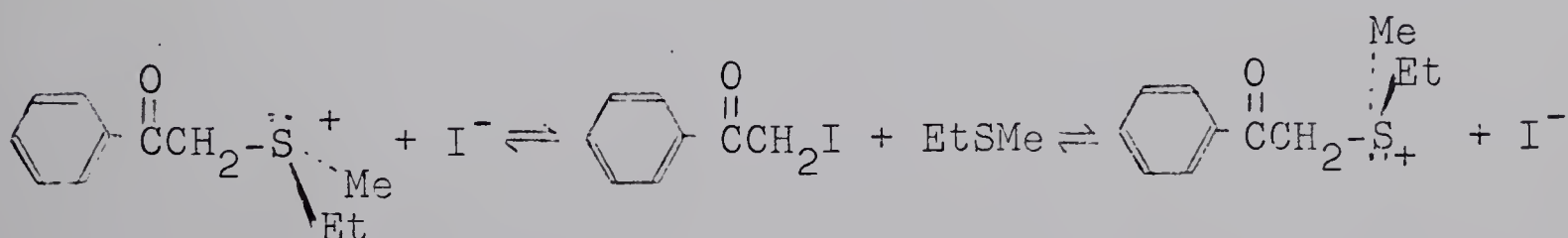




Carboxymethylethyl-    Phenacylethylmethyl-    2-p-Chlorophenacylthio-  
methylsulfonium ion    sulfonium ion    isochromanion ion

The l-isomer obtained as yellow crystals had a m.p.  $125^\circ$  and  $[\text{M}]_D -39.3$ , the d-isomer as bright yellow needles had a m.p.  $123^\circ$  and  $[\text{M}]_D +34.2$ . In 1945, Holliman and Mann (39) prepared the two optical isomers of 2-p-chlorophenacylthioisochromanion picrate by resolution of the bromocamphorsulfonate salt. The molecular rotations reported were  $[\text{M}]_D -243$  and  $[\text{M}]_D +250$ . The authors also noted that less than 5 per cent racemization occurred when the picrate was refluxed in ethanol for 7.5 hours.

The racemization of phenacylethylmethylsulfonium iodide was studied by Balfe, Kenyon and Phillips (40). They concluded that racemization involved a nucleophilic displacement on carbon by halide ion to produce inactive halide and sulfide followed by formation of the racemic salt.





To further elucidate the mechanism of solvolysis of sulfonium salts we have undertaken to resolve an asymmetric sulfonium ion and compare the rates of racemization and solvolysis in a variety of solvents as well as the reaction products.



## CHAPTER I

### t-BUTYLETHYLMETHYLSULFONIUM SALTS

t-Butylethylmethylsulfonium perchlorate was the first compound studied because it is the simplest trialkylsulfonium salt, containing an asymmetric sulfur atom, capable of forming a stable carbonium ion during solvolysis and because its behavior on solvolysis should be similar to that reported for t-butyldimethylsulfonium salts (1, 8-22). This chapter describes the synthesis and resolution of t-butylethylmethylsulfonium salts as well as the kinetics of their racemization and solvolysis. The results obtained will be discussed with reference to the following topics: the ratio of racemization to solvolysis, the effect of varying the anion, the effect of varying the ionic strength by increasing either the concentration of the sulfonium salt or by adding inert salt, solvent effects and temperature effects.

#### SYNTHESIS AND RESOLUTION

The route followed for the synthesis of t-butylethylmethylsulfonium perchlorate and other trialkylsulfonium salts is illustrated in Figure III. t-Butyl ethyl sulfide was











obtained from the acid-catalyzed addition of ethyl mercaptan to t-butyl alcohol. The procedure followed was a modification of the method used by Ipatieff and Pines for the preparation of t-butyl phenyl sulfide (41). Iodomethane adds readily to t-butyl ethyl sulfide to form the sulfonium iodide salt. Nitromethane is the preferred solvent because of its high dielectric and solvent properties. The reaction and workup should be carried out in the dark to prevent formation of iodine. In general, exchange of the anion of the sulfonium salt was accomplished by conversion to the hydroxide using a Dowex 1 x8 anion exchange resin in its hydroxide form followed by neutralization of the sulfonium hydroxide with the appropriate acid. The optically active salts were obtained by resolution of the 2R,3R-dibenzoylhydrogentartrate. The less soluble diastereomer was converted to the levorotary perchlorate salt by way of the hydroxide or, in the case of the t-butyl system, by metathesis with perchloric acid in a methanol-ethyl ether solution. Sulfonium salt enriched in the dextrorotary enantiomer was prepared in a similar manner from the mother liquors of the resolution. Properties of the t-butylethylmethylsulfonium salts prepared are shown in Table I.



TABLE I

PROPERTIES OF SOME t-BUTYLETHYLMETHYLSULFONIUM SALTS

Anion	Isomer	Melting point (decomp.)	$[\alpha]_D^{25}$
I <sup>-</sup>	dl	135.5	
dBHT <sup>-</sup> <sup>a</sup>	(-)	112.6	- 106 ( <u>c</u> 1.60, methanol)
ClO <sub>4</sub> <sup>-</sup>	dl	148	
ClO <sub>4</sub> <sup>-</sup>	(-)	148.6	- 34.6 ( <u>c</u> 1.51, methanol)
ClO <sub>4</sub> <sup>-</sup>	(+)	149	+ 27.5 ( <u>c</u> 3.66, methanol)
Br <sup>-</sup>	dl	121	
Br <sup>-</sup>	(-)	120	- 27.3 ( <u>c</u> 0.243, methanol)

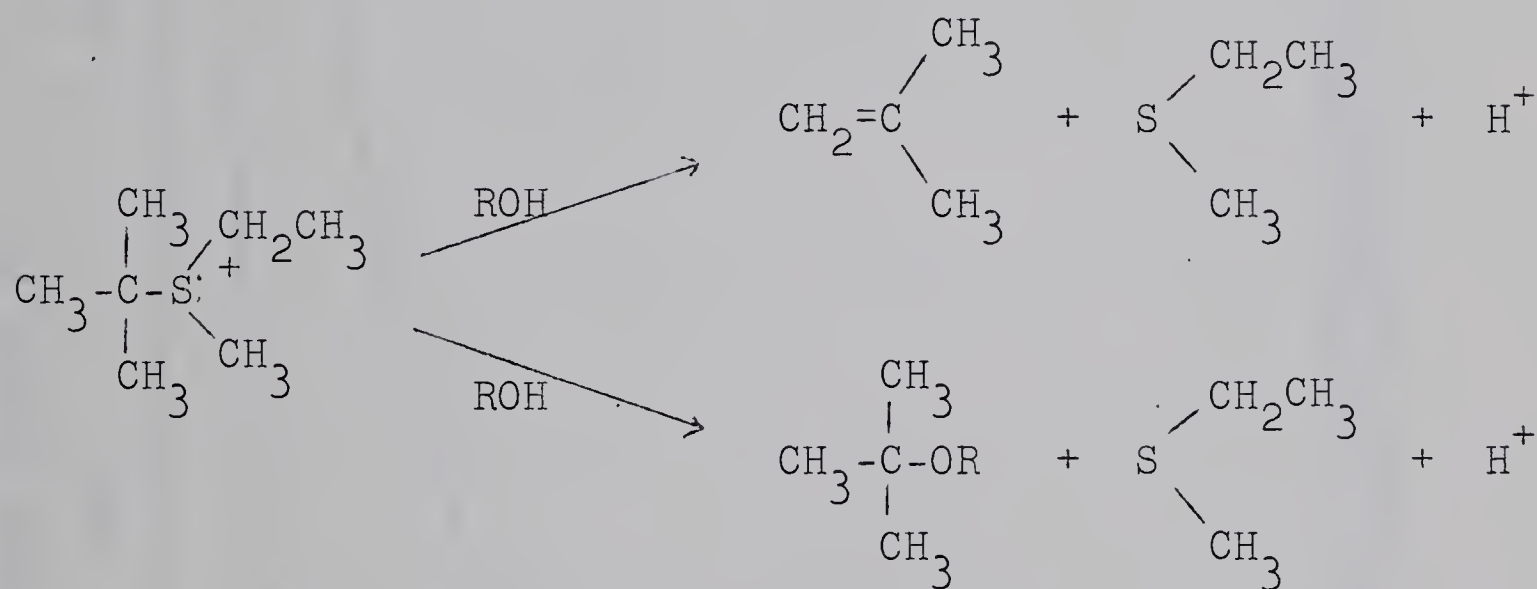
a) 2R,3R-Dibenzoylhydrogentartrate.

The n.m.r. and infrared spectra of the optical isomers were superimposable upon that of the corresponding racemic salt. All compounds gave satisfactory analyses. These are reported with the detailed synthetic procedure for each compound described in the Experimental section. Figure IV illustrates the variation of the specific rotation of (-)-t-butylethylmethylsulfonium perchlorate and 2R,3R-dibenzoylhydrogentartrate with changes in the wavelength of the incident light.



## RESULTS

The kinetics of the solvolysis of t-butylethylmethylsulfonium perchlorate were studied by following the rate of appearance of acid. Every mole of sulfonium salt produces upon solvolysis one mole of acid whether elimination or substitution occurs.



The reactions follow first-order kinetics. The titrimetric rate constants,  $k_t$ , were calculated from the relationship:

$$kt = 2.303 \log. \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

where  $V_t$  is the titer at time  $t$ . Reactions were usually followed to ca. 85 per cent completion and a good straight line was obtained when the logarithm of  $(V_{\infty} - V_t)$  was plotted





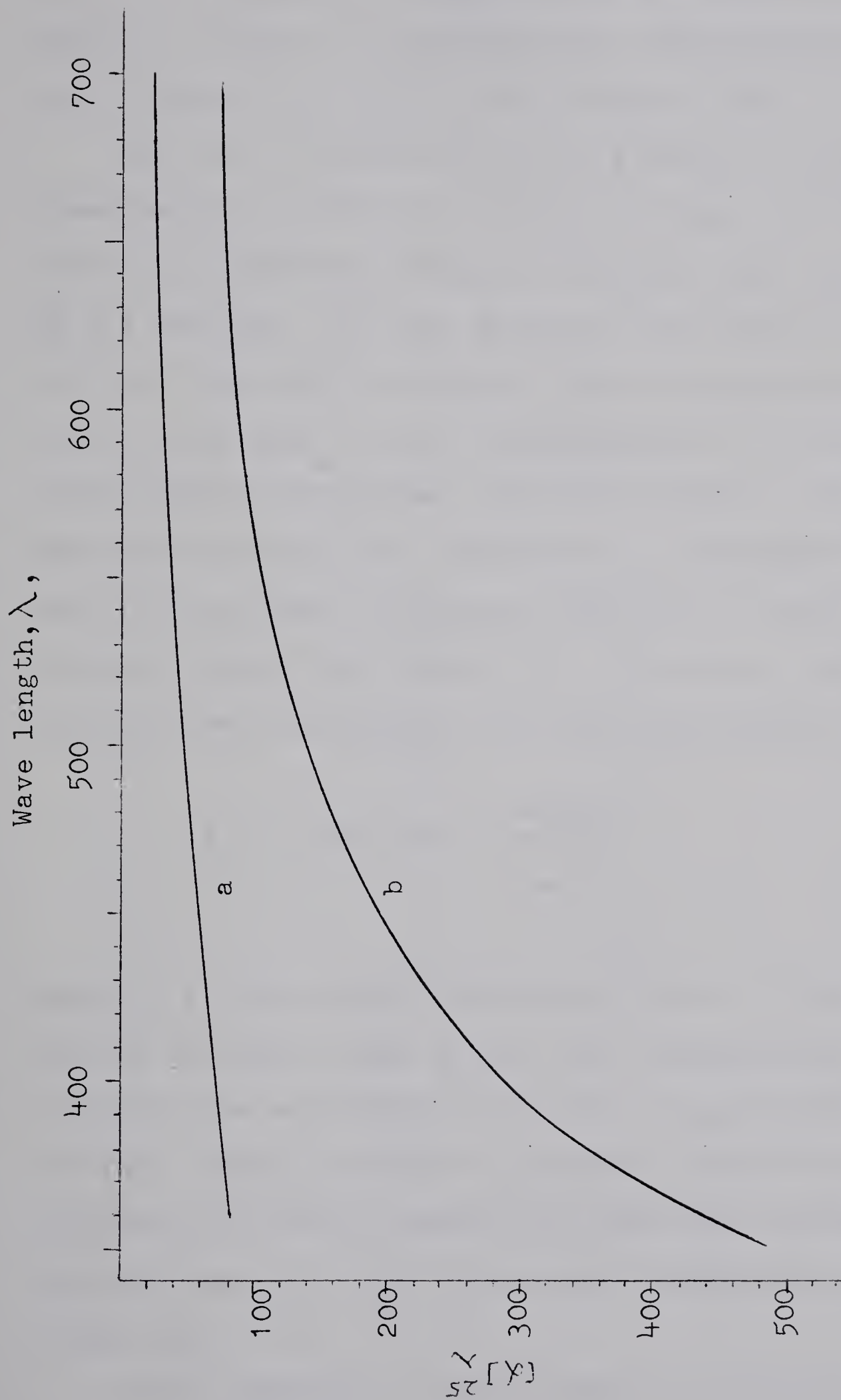


Figure IV. Specific rotation of (-)-t-butylethylmethylsulfonium perchlorate (a) and (-)-2R,3R-dibenzoylhydrogentartrate (b) vs wavelength of the incident light.



vs time. A typical titrimetric rate analysis is shown in Table II. Figure V illustrates the corresponding kinetic plot of  $\log. (V_{\infty} - V_t)$  vs time for Run 3-230.

The rate of racemization was studied by following the disappearance of optical rotation vs time. A Perkin-Elmer Model 141 Polarimeter using an incident light beam of 436 mμ was employed. At this wavelength the optical rotation is larger than at the sodium D line, thus permitting a greater precision in rate determinations. At first, a sealed ampoule method was employed (Method I), but later the entire reaction was conducted in a thermostated polarimetric tube using a Honeywell Recorder to record the rotation versus time (Method II). The first-order rate constants were calculated from the relationship:

$$k_t = 2.303 \log. \frac{\alpha_{\infty} - \alpha_0}{\alpha_{\infty} - \alpha_t}$$

where  $\alpha_t$  is the optical rotation at time t. Reactions were usually followed to ca. 85 per cent completion and a good straight line was obtained when  $\log. (\alpha_{\infty} - \alpha_t)$  was plotted vs time. Typical examples of Methods I and II are shown in Tables III and IV respectively and their corresponding plots of  $\log. (\alpha_{\infty} - \alpha_t)$  vs time are illustrated in Figures VI and VII.

In all solvents, a finite amount of solvolysis of the



TABLE II

SOLVOLYSIS OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE  
(0.03358 M) IN ANHYDROUS ETHYLENE GLYCOL AT 50.00°. RUN 3-230

Aliquot: 4.947 ml. Titrant: NaOCH<sub>3</sub>, 0.04157 M. Indicator:  
Phenolphthalein. Blank: 0.036 ± 0.002 ml. Theoretical  
infinity titer: 3.902 ml.

Time, (sec.)	Titer, (ml.)	log (V <sub>∞</sub> - V <sub>t</sub> )	10 <sup>5</sup> k <sub>t</sub> <sub>1</sub> (sec. <sup>-1</sup> )
0	0.166	0.5642	
5400	0.694	0.4967	2.87
10200	1.106	0.4355	2.91
14400	1.430	0.3806	2.94
18000	1.684	0.3320	2.97
22800	1.976	0.2686	2.99
27000	2.206	0.2111	3.01
32400	2.440	0.1436	2.99
39600	2.704	0.0523	2.98
50400	2.998	1.9212	2.94
63000	3.255	1.7612	2.93
25200 a	3.829		
37800 a	3.836		
48600 a	3.832		
			Average 2.95 ± 0.04

a) Temperature: 70.00°; V<sub>∞</sub> = 3.833 ± 0.003 ml., 98 per cent  
of the theoretical infinity.



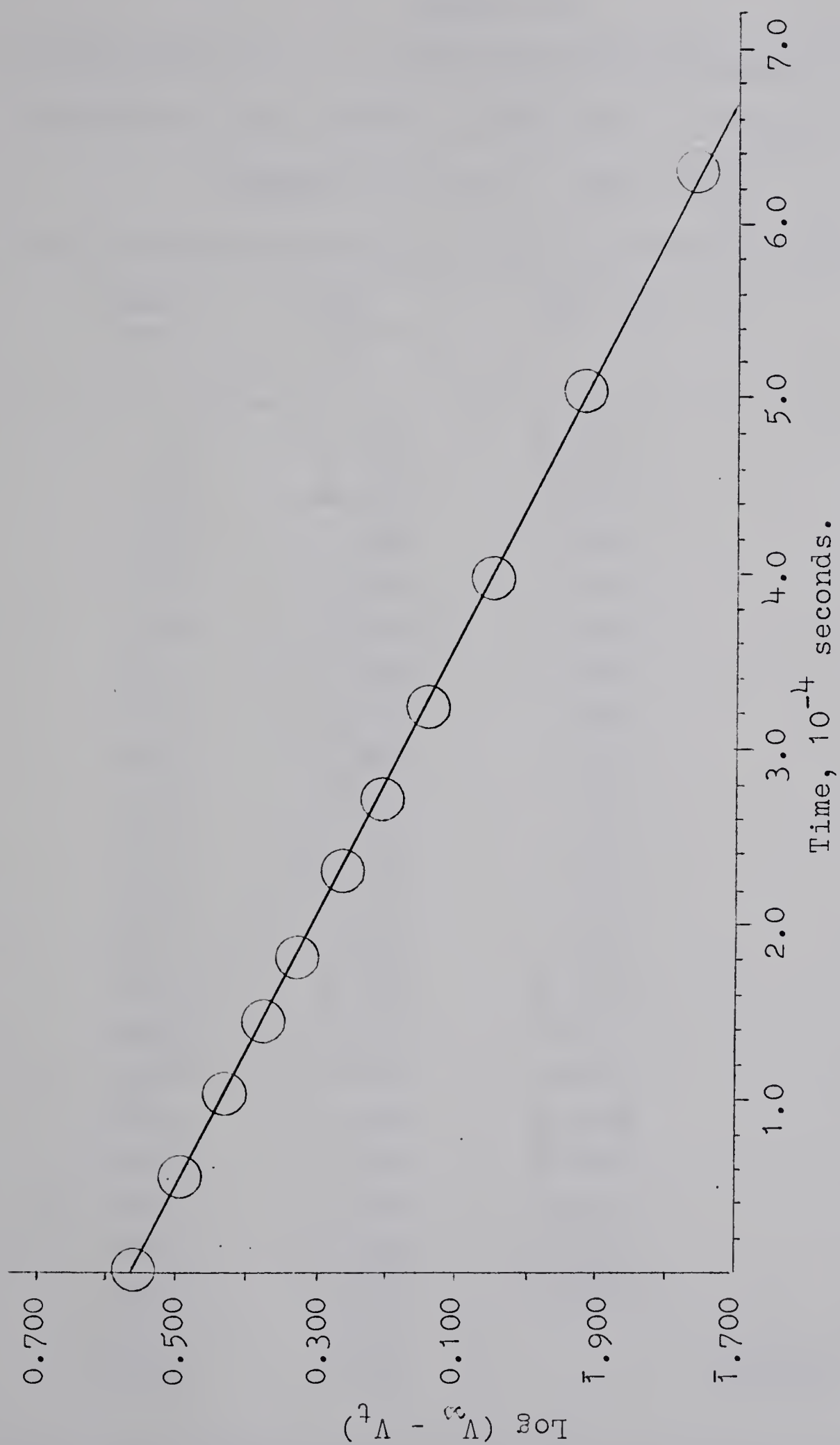


Figure V.  $\text{Log}(V_\infty - V_t)$  vs time, for the solvolysis of t-butylethylmethylsulfonium perchlorate (0.03358 M) in anhydrous ethylene glycol at  $50.00^\circ$ . Run 3-230





TABLE III

RACEMIZATION OF (-)-t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE  
(0.02373 M) WITH ADDED 2,6-LUTIDINE (0.05100 M) IN ANHYDROUS  
ACETONE AT 50.00°. RUN 2-229

Time, (sec.)	$\alpha_{436}^{25^\circ}$ $\mu$	$\log (\alpha_0 - \alpha_t)$	$10^4 k_{\alpha}$ (sec. <sup>-1</sup> )
0	-0.296	1.4713	
180	-0.272	1.4346	4.70
360	-0.254	1.4048	4.26
540	-0.229	1.3598	4.76
720	-0.212	1.3263	4.64
900	-0.199	1.2989	4.41
1080	-0.179	1.2529	4.66
1260	-0.166	1.2201	4.59
1500	-0.149	1.1732	4.58
1740	-0.127	1.1038	4.86
1980	-0.119	1.0755	4.60
2220	-0.107	1.0294	4.59
2460	-0.099	2.9996	4.42
2880	-0.075	2.8751	4.77
3120	-0.072	2.8573	4.53
3420	-0.069	2.8388	4.26
3720	-0.049	2.6902	4.84
4260	-0.043	2.6335	4.53
4860	-0.029	2.4757	4.72
5340	-0.025	2.3979	4.63
24000	0.001		
42000	0.000		
			Average 4.60 $\pm$ 0.13



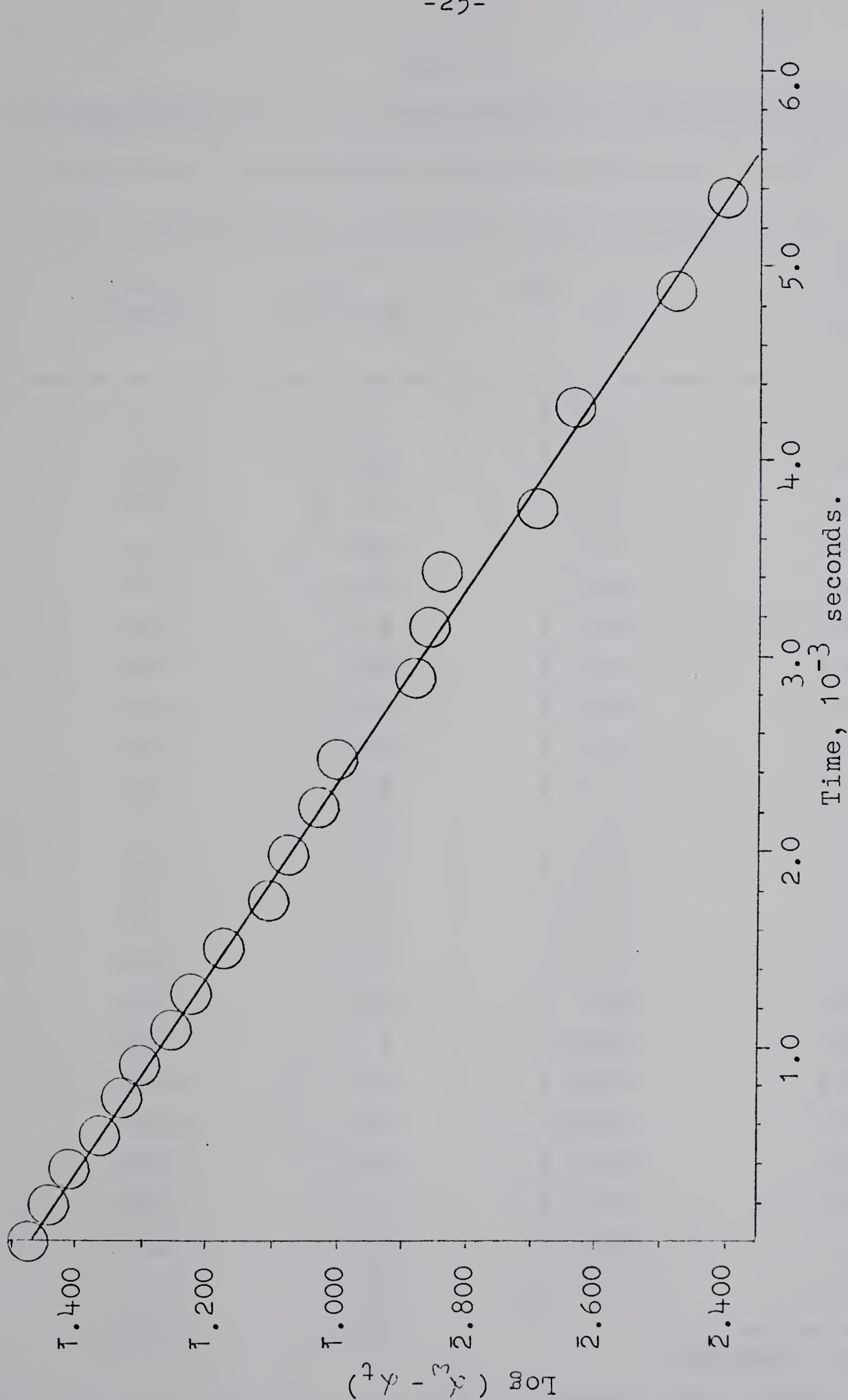


Figure VI.  $\text{Log } (\alpha_t - \alpha_0)$  vs time for the racemization of (-)-*t*-butylethylmethylsulfonium perchlorate (0.02373 M) with added 2,6-lutidine (0.05100 M) in anhydrous acetone at 50.00°. Run 2-229.



TABLE IV

RACEMIZATION OF (-)-t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE  
(0.03300 M) IN ANHYDROUS ETHYLENE GLYCOL AT 50.00°. RUN 3-233

Time, (sec.)	$\alpha_{436}^{50^\circ}$ mμ	$\log (\alpha_{\infty} - \alpha_t)$	$10^4 k$ (sec. <sup>-1</sup> )
0	-0.411	1.6138	
120	-0.392	1.5933	3.93
240	-0.375	1.5740	3.82
360	-0.359	1.5551	3.75
510	-0.337	1.5276	3.90
660	-0.319	1.5038	3.84
840	-0.298	1.4742	3.83
1020	-0.277	1.4425	3.87
1260	-0.252	1.4014	3.88
1500	-0.228	1.3579	3.93
1740	-0.208	1.3181	3.91
1980	-0.190	1.2788	3.90
2220	-0.173	1.2380	3.90
2520	-0.156	1.1931	3.85
2820	-0.138	1.1399	3.87
3240	-0.117	1.0682	3.88
3660	-0.100	1.0000	3.86
4080	-0.084	2.9243	3.89
4680	-0.067	2.8261	3.88
5400	-0.052	2.7160	3.83
6240	-0.038	2.5798	3.82
7320	-0.026	2.4150	3.77
42000	0.000		
			Average 3.86 ± 0.04



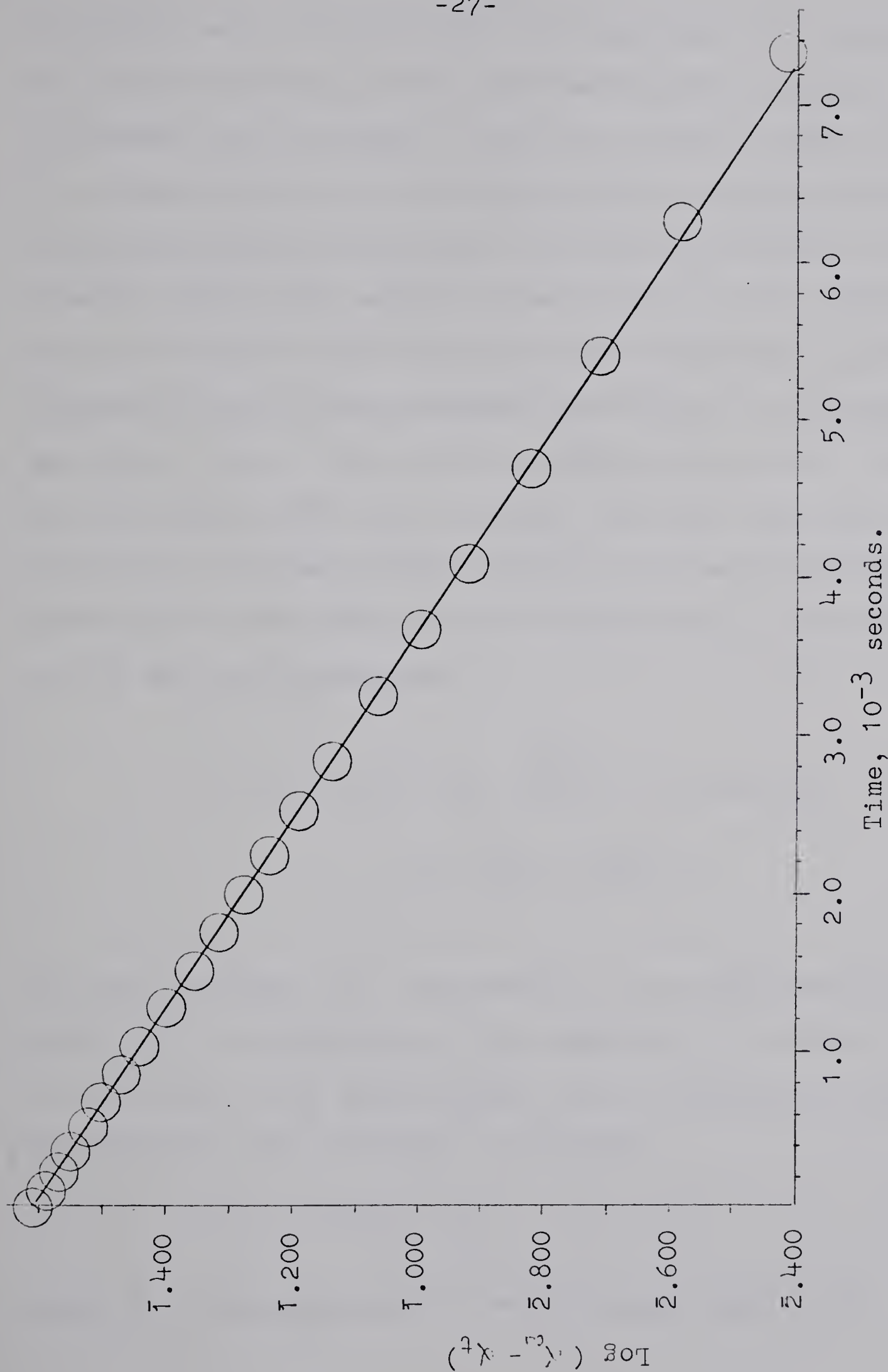
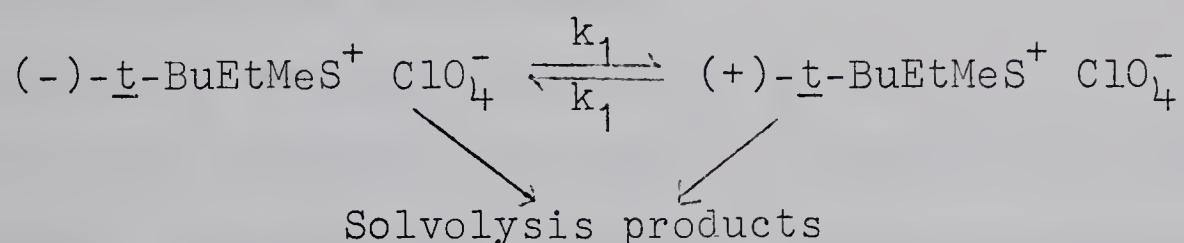


Figure VII.  $\text{Log } (\alpha_c - \alpha_t)$  vs time for the racemization of (-)-t-butylethylmethylsulfonium perchlorate (0.03300 M) in anhydrous ethylene glycol at  $50.00^\circ$ . Run 3-233.





sulfonium salt occurred under the conditions of racemization. The relative ratios of the polarimetric rate constant to the titrimetric rate constant,  $k_x/k_t$ , are shown in Table XII. The largest amount of solvolysis occurring during racemization was observed in acetone, the smallest in water. For example, during the period of measurement of the polarimetric rate in acetone at  $50^\circ$  (90 per cent racemization), t-butyl-ethylmethyisulfonium perchlorate solvolyzes to an extent of ca. 23 per cent. (Runs 2-216, 2-229 in Table VI). In water at  $50^\circ$  (Runs 2-212, 2-225 in Table VI), ca. 8 per cent solvolysis occurred during the period of measurement of the polarimetric rate (80 per cent racemization). The effect at  $25^\circ$  was less pronounced.



The rate constant,  $k_1$ , the specific first-order rate constant for the conversion of one enantiomer to another as illustrated in the above scheme, can be calculated from the observed rate constants as follows:

$$k_1 = \frac{1}{2} (k_x - k_t)$$

where  $k_x$  is the polarimetric rate constant and  $k_t$  the



titrimetric rate constant. The values of  $k_1$  for the solvolysis of t-butylethylmethylsulfonium perchlorate are also presented in Tables V, VI, and VII.

There are a number of noteworthy features in Table V. Decreasing the temperature has a greater effect on the rate of solvolysis than on the rate of racemization. The half-lives for the ethanolysis of t-butylethylmethylsulfonium perchlorate are 4.3 hours and 226 hours at 50° and 25° respectively. The relative values of the rate constants at 50° and 25° are  $k_t : k_d : k_1$  as 1 : 10.5 : 4.7 and 1 : 18 : 8.3 respectively. Changing the ionic strength by increasing the concentration of the sulfonium salt or by adding inert salt has little or no effect on either the rate of racemization or solvolysis.

The effect of varying the solvent on the rates of racemization and solvolysis, as shown in Tables VI and VII, are very small. The fastest titrimetric rate was observed in acetone and the slowest in water, however the range is less than a factor of 4. The effect of solvent variation on the rate of racemization was even smaller.

An experiment was conducted to establish that the excess loss of optical activity was due to racemization and not decomposition of the substrate (Run 1-97). An ethanolic solution of (-)-t-butylethylmethylsulfonium perchlorate was kept at 25° until the optical rotation had



TABLE V

SOLVOLYSIS OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE IN  
ANHYDROUS ETHANOL

Run	Temp. (°C.)	Isomer	Conc. (M.)	$\mu$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_{\alpha}^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )
1-125	50	d1	0.01184	0.015	44.9 ± 1.2		
2-99	50	(-)	0.01187	0.015	45.1 ± 0.6	471 ± 15	213 ± 8
2-97	50	(+)	0.01198	0.015	46.7 ± 0.4	452 ± 21	202 ± 10
2-91	50	d1	0.002358	0.003	47.0 ± 2.6		
2-107	50	(-)	0.002343	0.003		485 ± 69	219 ± 37
2-89	50	d1	0.02390	0.030	45.5 ± 0.4		
2-101	50	(-)	0.02374	0.030		443 ± 15	198 ± 8
2-93 <sup>d</sup>	50	d1	0.01195	0.029	46.3 ± 0.9		
2-109 <sup>d</sup>	50	(-)	0.01187	0.029		457 ± 15	208 ± 8
2-95 <sup>e</sup>	50	d1	0.01195	0.30	44.5 ± 0.5		
2-111 <sup>e</sup>	50	(-)	0.01187	0.30		448 ± 7	202 ± 4
4-54 <sup>f</sup>	50	(-)	0.02335	0.030	43.4 ± 1.7	480 ± 17	219 ± 9
1-48	25	d1	0.02086	0.027	0.852 ± 0.026		
2-103	25	(-)	0.02374	0.030		14.9 ± 0.4	7.0 ± 0.2
1-71	25	d1	0.01209	0.015	0.857 ± 0.015		
2-201	25	(-)	0.01187	0.015		15.2 ± 1.3	7.2 ± 0.6
1-125	70	d1	0.01184	0.015	728 ± 50		
1-127	70	(-)	0.009695	0.012	723 ± 43		

a) Titrimetric rate constant; b) polarimetric rate constant, run 4-54 was done by Method II and all the others by Method I (see experimental section); c)  $k_1 = \frac{1}{2} (k_{\alpha} - k_t)$ ; d) 0.01114 M. added lithium perchlorate; e) 0.2220 M. added lithium perchlorate; f) 0.4335 M. added methyl sulfide and 0.0500 M. added 2,6-lutidine.





TABLE VI

SOLVOLYSIS OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE IN A VARIETY OF SOLVENTS AT 50.00°.

Run	Solvent	Isomer	Conc. (M.)	$\mu$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_x^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )
2-89	EtOH	d1	0.02390	0.030	45.5±0.4		
2-101	EtOH	(-)	0.02374	0.030		443±15	198±8
2-99	EtOH	(-)	0.01187	0.015	45.1±0.6	471±15	213±8
1-123	HOAc <sup>d</sup>	d1	0.01462	0.042	36.2±1.0		
2-193	HOAc <sup>d</sup>	(-)	0.01429	0.042		413±17	189±9
1-153	HOAc <sup>e</sup>	d1	0.1472	0.42	27.4±0.2		
1-143	HOAc <sup>e</sup>	(-)	0.1472	0.42		390±6	182±3
1-137	50%AcOAc <sup>df</sup>	d1	0.01517	0.042	26.3±0.3		
2-197	50%AcOAc <sup>df</sup>	(-)	0.01442	0.042		439±19	207±9
2-212	H <sub>2</sub> O	d1	0.02990	0.030	16.6±0.2		
2-225	H <sub>2</sub> O	(-)	0.02999	0.030		283±18	133±9
2-216	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>g</sup>	d1	0.02370	0.030	55.9±1.1		
2-229	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>g</sup>	(-)	0.02373	0.030		460±13	202±7
3-107	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>g</sup>	d1	0.01187	0.015	54.7±1.2		
3-155	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>g</sup>	(-)	0.01201	0.015		481±10	213±6
2-233	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>g</sup>	(-)	0.04742	0.060		461±17	203±9
3-230	HOCH <sub>2</sub> CH <sub>2</sub> OH	d1	0.03358	0.030	29.5±0.4		
3-234	HOCH <sub>2</sub> CH <sub>2</sub> OH	(-)	0.03300	0.030		386±4	178±2

a) Titrimetric rate constant; b) polarimetric rate constant, runs in book 3 were done by Method II and all the others by Method I (see experimental section); c)  $k_1 = \frac{1}{2} (k_x - k_t)$ ; d) 0.0293 M. added sodium acetate; e) 0.293 M. added sodium acetate; f) 50 volume per cent AcOAc in HOAc; g) 0.051 M. added 2,6-lutidine.





TABLE VII

SOLVOLYSIS OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE IN A  
VARIETY OF SOLVENTS AT 25.00°.

Run	Solvent	Isomer	Conc. (M.)	$\mu$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_{\lambda}^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )
1-48	EtOH	d1	0.02086	0.027	0.852±0.026		
2-103	EtOH	(-)	0.02374	0.030		14.0±0.4	6.6±0.2
1-121	HOAc <sup>d</sup>	d1	0.01445	0.042	0.657±0.014		
2-195	HOAc <sup>d</sup>	(-)	0.01429	0.042		13.7±0.6	6.5±0.3
2-203	50%AcOAc <sup>de</sup>	d1	0.01441	0.042	0.451±0.008		
2-199	50%AcOAc <sup>de</sup>	(-)	0.01442	0.042		13.8±0.7	6.7±0.3
2-211	H <sub>2</sub> O	d1	0.02990	0.030	0.256±0.002		
2-227	H <sub>2</sub> O	(-)	0.02999	0.030		8.43±0.59	4.1±0.3
2-215	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	d1	0.02370	0.030	1.06±0.05		
2-231	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	(-)	0.02373	0.030		14.2±0.5	6.6±0.3
3-109	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	d1	0.01187	0.015	1.05±0.02		
3-159	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	(-)	0.01217	0.015		13.3±0.4	6.1±0.2
2-236	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	(-)	0.04742	0.060		14.4±0.4	6.7±0.2
1-211	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>fh</sup>	d1	0.04006	0.20	1.09±0.02		
1-213	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>gh</sup>	d1	0.04044	0.20	1.16±0.02		
3-231	HOCH <sub>2</sub> CH <sub>2</sub> OH	d1	0.03358	0.030	0.531±0.012		
3-236	HOCH <sub>2</sub> CH <sub>2</sub> OH	(-)	0.03300	0.030		10.2±0.1	4.8±0.1

a) Titrimetric rate constant; b) polarimetric rate constant, runs in book 3 were done by Method II, all others by Method I (see experimental section); c)  $k_1 = \frac{1}{2} (k_{\lambda} - k_t)$ ; d) 0.0293 M. added sodium acetate; e) 50 volume per cent acetic anhydride in acetic acid; f) 0.051 M. added 2,6-lutidine; g) 0.166 M. added 2,6-lutidine; h) 0.1194 M. added lithium perchlorate.



decreased to zero. The melting point, n.m.r. and infrared spectra of the crystals isolated from the reaction mixture were identical with that of authentic dl-t-butylethylmethylsulfonium perchlorate. Details of the experiment are given at the end of the chapter.

In Run 4-54 (Table V) a twenty fold molar excess of dimethyl sulfide was added to a solution of (-)-t-butylethylmethylsulfonium perchlorate in ethanol. The rates of solvolysis and racemization at 50° are the same, within experimental error, as those in the absence of dimethyl sulfide (Run 2-99, Table V). When the optical rotation had decreased to zero (corresponding to 0.5 half-lives of solvolysis), the solvent of a 25 ml. aliquot was removed. No significant amount of t-butyldimethylsulfonium perchlorate could be detected by n.m.r. The spectra of the recovered and starting materials were identical within experimental error. Therefore under the conditions of racemization in ethanol t-butylethylmethylsulfonium perchlorate does not significantly exchange sulfide.

In the case of t-butylethylmethylsulfonium bromide solvolysis, the HBr produced reacts slowly with the ethanol solvent. To prevent this an excess of 2,6-lutidine was added to the reaction solution in order to neutralize the acid produced. 2,6-Lutidine was chosen as the base because its conjugate acid, 2,6-lutidinium bromide, can be titrated



with sodium methoxide using phenolphthalein as indicator. The 2,6-dimethyl groups will hinder any nucleophilic attack of the base on the substrate (43). Good first order kinetics were obtained for these reactions as shown for run 3-221, described in Table VIII and Figure VIII. The rates of solvolysis and racemization of t-butylethylmethylsulfonium bromide in variety of solvents are presented in Table IX.

A comparison of Tables VI and IX reveals that ethanolysis of t-butylethylmethyl sulfonium bromide at 50° is 30 per cent faster than ethanolysis of the corresponding perchlorate; acetolysis of the bromide is 20 per cent faster and the rates of solvolysis in 50 volume per cent acetic anhydride-acetic acid are the same within experimental error. The observed polarimetric rate constants for (-)-t-butylethylmethylsulfonium bromide at 50° are 20 per cent larger than that of the corresponding perchlorate in the three solvents investigated. The effects of changing the anion are less at 25°.

2,6-Lutidine was also added to the reaction solution for runs conducted in acetone in order to prevent acid-catalyzed decomposition of the solvent. 2,6-Lutidinium perchlorate can be titrated with standard base using phenolphthalein as indicator (42). Run 2-216, presented in Table X and Figure XI, is a typical rate analysis in acetone to show that these follow good first-order kinetics.





TABLE VIII

SOLVOLYSIS OF (-)-t-BUTYLETHYLMETHYLSULFONIUM BROMIDE  
(0.01150 M) WITH ADDED 2,6-LUTIDINE (0.05080 M) IN ANHYDROUS  
ETHANOL AT 50.00°. RUN 3-221.

Aliquot: 4.947 ml. Titrant: NaOCH<sub>3</sub>, 0.04257 M. Indicator:  
phenolphthalein. Blank: 0.028 ± 0.002 ml. Theoretical  
titer: 1.336 ml.

Time, (sec.)	Titer, (ml.)	log (V <sub>∞</sub> - V <sub>t</sub> )	10 <sup>5</sup> k <sub>t1</sub> (sec. <sup>-1</sup> )
0	0.117	0.0810	
3600	0.345	1.9899	5.83
5100	0.428	1.9513	5.86
7200	0.532	1.8976	5.87
9600	0.637	1.8357	5.88
12000	0.732	1.7709	5.95
15000	0.822	1.6990	5.86
18000	0.908	1.6170	5.94
21600	0.984	1.5289	5.89
27000	1.071	1.3927	5.87
32400	1.145	1.2480	5.92
37800	1.191	1.1173	5.87
194400	1.311		
266400	1.334		Average 5.89 ± 0.03

V<sub>∞</sub> = 1.323 ± 0.012 ml., 99 per cent of the theoretical  
infinity.





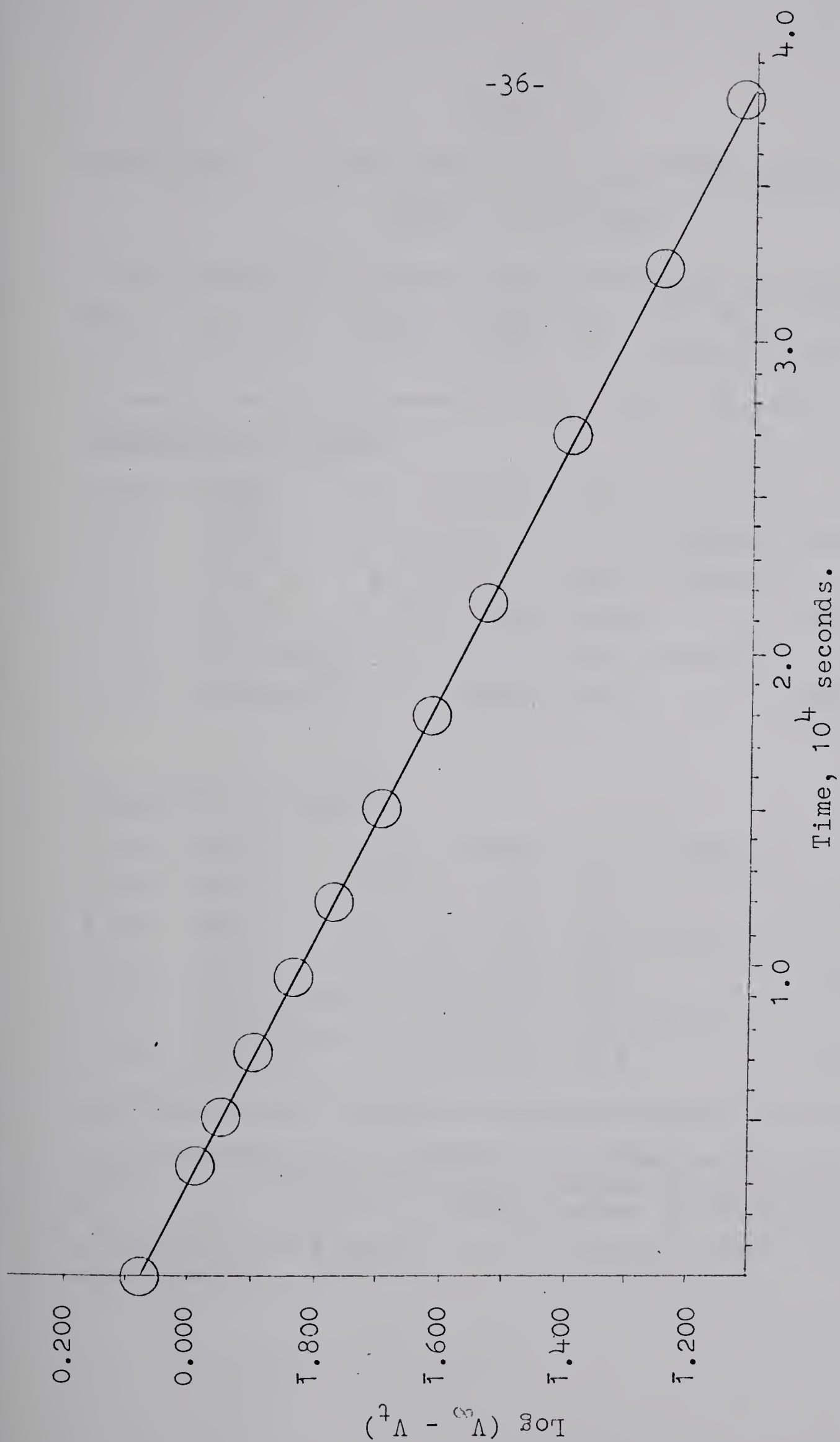


Figure VIII.  $\text{Log } (V_{\infty} - V_t)$  vs time for the solvolysis of (-)-t-butylethylmethylsulfonium bromide (0.01150 M) with added 2,6-lutidine (0.05080 M) in anhydrous ethanol at 50.00°. Run 3-221.



TABLE IX

SOLVOLYSIS OF t-BUTYLETHYLMETHYLSULFONIUM BROMIDE IN A  
VARIETY OF SOLVENTS

Run	Solvent	Isomer	Conc. (M.)	$\mu$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_d^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )
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Temperature: 50.00°.

3-199	EtOH <sup>d</sup>	d1	0.01203	0.015	57.5±0.9		
3-221	EtOH <sup>d</sup>	(-)	0.01150	0.015	58.9±0.3	574±11	208± 6
3-91	HOAc <sup>e</sup>	d1	0.01486	0.042	43.6±2.0		
3-238	HOAc <sup>e</sup>	(-)	0.01486	0.042		496± 4	226± 3
3-99	50%AcOAc <sup>ef</sup>	d1	0.01477	0.042	25.9±3.5		
3-183	50%AcOAc <sup>ef</sup>	(-)	0.01527	0.042		504± 8	239± 6.

Temperature: 25.00°.

3-201	EtOH <sup>d</sup>	d1	0.01203	0.015	1.09±0.04		
3-225	EtOH <sup>d</sup>	(-)	0.01150	0.015		13.9±0.5	6.4±0.3
3-93	HOAc <sup>e</sup>	d1	0.01486	0.042	0.831 ±0.050		
3-240	HOAc <sup>e</sup>	(-)	0.01486	0.042		13.2±0.5	6.2±0.3
3-101	50%AcOAc <sup>ef</sup>	d1	0.01477	0.042	0.537±0.023		
3-185	50%AcOAc <sup>ef</sup>	(-)	0.01527	0.042		12.6±0.3	6.1±0.2

a) Titrimetric rate constant; b) polarimetric rate constant  
obtained by Method II (see experimental section); c)  
 $k_1 = \frac{1}{2} (k_x - k_t)$ ; d) 0.0508 M added 2,6-lutidine; e) 0.0293  
M added sodium acetate; f) 50 volume per cent acetic anhydride-  
acetic acid.



TABLE X

SOLVOLYSIS OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE  
(0.02370 M) WITH ADDED 2,6-LUTIDINE (0.05100 M) IN  
ANHYDROUS ACETONE AT 50.00°. RUN 2-216.

Aliquot: 4.93<sup>4</sup> ml. Titrant: NaOCH<sub>3</sub>, 0.03<sup>4</sup>71 M. Indicator:  
phenolphthalein. Blank: 0.038 ml. Theoretical infinity  
titer: 3.370 ml.

Time, (sec.)	Titer, (ml.)	Log (V <sub>∞</sub> - V <sub>t</sub> )	10 <sup>5</sup> k <sub>t1</sub> (sec. <sup>-1</sup> )
0	0.087	0.5333	
1800	0.426	0.4879	5.81
3600	0.727	0.4431	5.77
5400	0.968	0.4036	5.53
7200	1.241	0.3541	5.73
9900	1.525	0.2958	5.53
12600	1.813	0.2274	5.59
19020	2.307	0.0770	5.52
24000	2.580	1.9643	5.46
28800	2.786	1.8543	5.43
34200	2.991	1.7076	5.56
7200 <sup>a</sup>	3.493		
14400 <sup>a</sup>	3.509		
			Average 5.59 ± 0.11

a) Temperature 70.00°; V<sub>∞</sub> = 3.501 ± 0.008 ml., 103 per cent  
of the theoretical infinity.



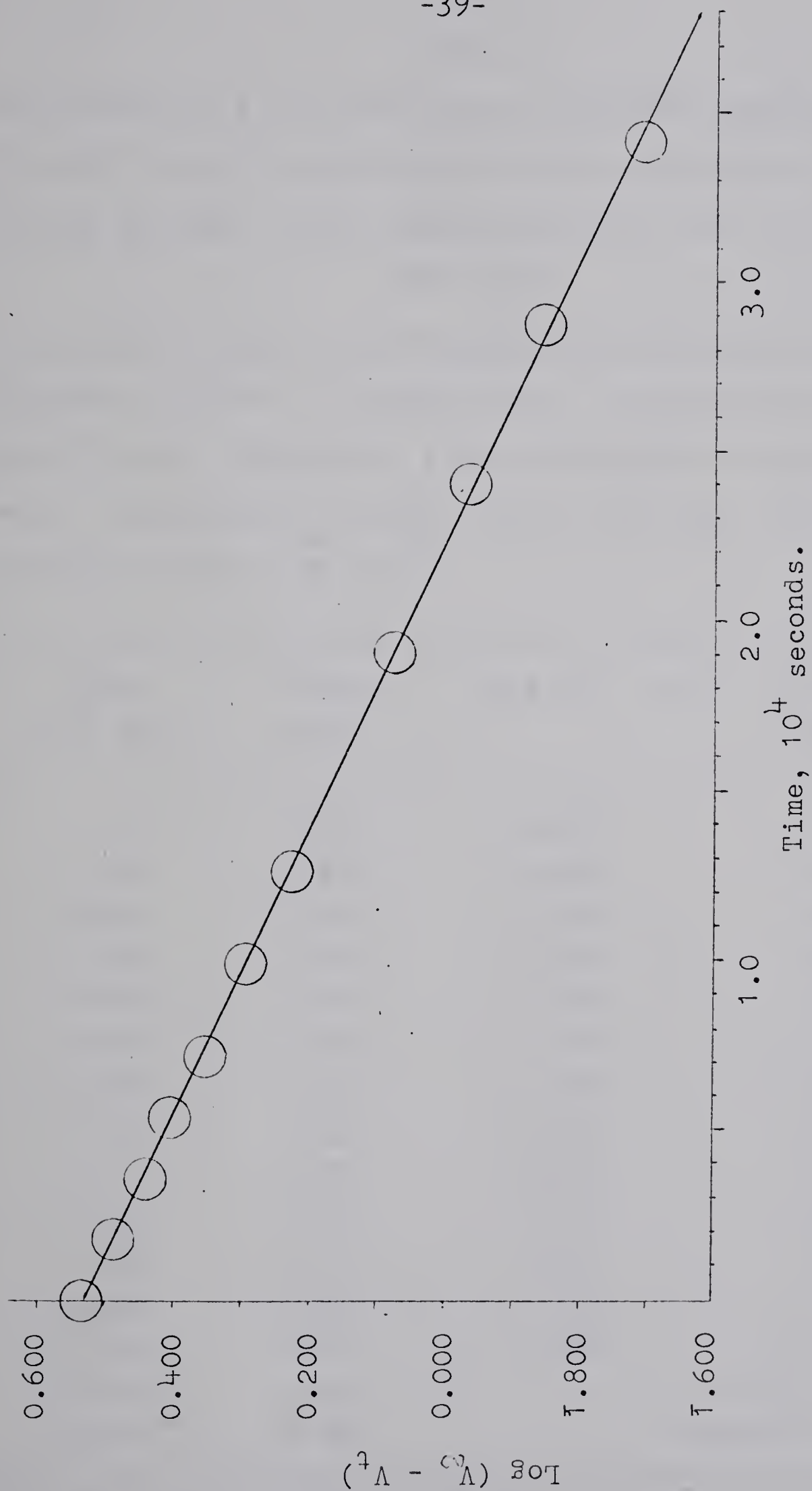


Figure IX.  $\text{Log}(V_{\infty} - V_t)$  vs time for the solvolysis of *t*-butylethylmethylsulfonium perchlorate (0.02370 M) with added 2,6-lutidine (0.0510 M) in anhydrous acetone at 50.00°. Run 2-216.





TABLE XI

SOLVOLYSIS OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE  
(0.01441 M) WITH ADDED SODIUM ACETATE (0.02935 M) IN 50  
VOLUME PER CENT ACETIC ANHYDRIDE-ACETIC ACID AT 25.00°.  
RUN 2-203.

Aliquot: 4.934 ml. Titrant:  $\text{HClO}_4$ , 0.03576 M in glacial  
acetic acid. Indicator: p-naphtholbenzein in glacial acetic  
acid. Theoretical initial titer: 4.049 ml. Theoretical  
infinity titer: 2.061 ml.

Time, ( $10^6$ sec.)	Titer, (ml.)	Log ( $V_t - V_\infty$ )	$10^7 k_{t-1}$ (sec. $^{-1}$ )
0	4.011	0.2871	
0.1704	3.874	0.2553	4.30
0.2664	3.792	0.2350	4.50
0.3990	3.689	0.2082	4.56
0.5184	3.605	0.1850	4.54
0.7920	3.428	0.1316	4.52
0.9792	3.341	0.1028	4.33
1.1388	3.230	0.0630	4.53
1.3842	3.081	0.0030	4.73
1.8036	2.929	1.9320	4.53
2.1672	2.792	1.8561	4.58
2.9016	2.591	1.7135	4.55
3.5700	2.471	1.5988	4.44
0.2664 <sup>a</sup>	2.076		
0.3960 <sup>a</sup>	2.072		
			Average 4.51 $\pm$ 0.08

a) Temperature: 70.00°;  $V_\infty = 2.074 \pm 0.002$  ml., 97 per cent  
of the theoretical infinity.



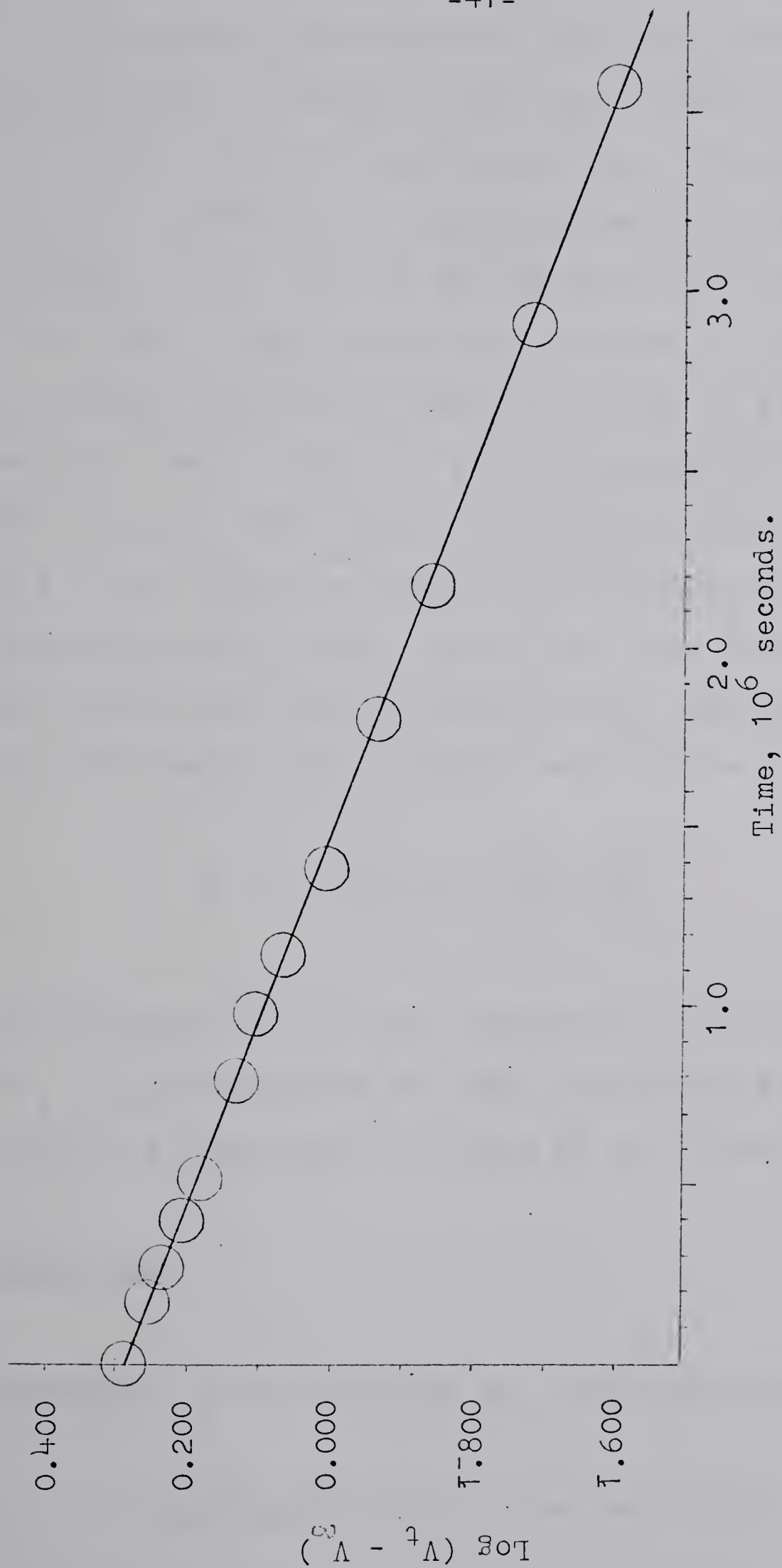


Figure X.  $\text{Log } (V_t - V_\infty)$  vs time for the solvolysis of t-butylethylmethylsulfonium perchlorate (0.01441 M) with added sodium acetate (0.02935 M) in 50 volume per cent acetic anhydride-acetic acid at 25.00°. Run 2-203.



In acetic acid and acetic anhydride-acetic acid solvent mixtures the titrimetric rate was followed in the presence of a molar excess of sodium acetate. Solvolysis in acetic acid in the absence of added base at 70° essentially ceases when ca. 17 per cent of the sulfonium salt has reacted (Run 1-85). Each aliquot was titrated for excess base using a standard solution of perchloric acid in glacial acetic acid to the greenish end point of p-naphtholbenzein (44). The end point was sharp in all cases except for the solvolysis of the sulfonium bromide in 50 volume per cent acetic anhydride-acetic acid. Since the titer decreases with time, the first-order kinetic relationship employed to calculate the titrimetric rate constant was modified as follows:

$$kt = 2.303 \log. \frac{V_o - V_{\infty}}{V_t - V_{\infty}}$$

Good straight lines were obtained when the logarithm of  $(V_t - V_{\infty})$  was plotted vs time. A typical analysis, Run 2-203, is illustrated in Table XI and Figure X.

## DISCUSSION

### Comparison of Racemization and Solvolysis Rates

t-Butylethylmethylsulfonium perchlorate racemizes faster



than it solvolyzes. At 50°, the polarimetric rate is between 8 and 17 times faster than the solvolysis rate, at 25° it is between 13 and 33 times faster depending upon the solvent. A summary of the relative rates is presented in Table XII.

The ratio of the rate constants of racemization to the rate constants of solvolysis varies from one solvent to another since solvolysis is affected more by change in medium than racemization. Since the activation energy for solvolysis is greater than that for racemization (Table XIV), the ratio of the polarimetric rate constant to the titrimetric rate constant,  $k_p/k_t$ , increases as the temperature is decreased.

Recovery of racemic starting material (Run 1-97) establishes that the excess loss of optical activity of t-butylethylmethylsulfonium perchlorate in ethanol was due to racemization of the substrate and not its decomposition.

The racemization of sulfonium perchlorate salts cannot involve a reversible nucleophilic displacement on carbon as shown by Kenyon et al. (40) for the racemization of phenacylmethylsulfonium iodide because the perchlorate anion is non-

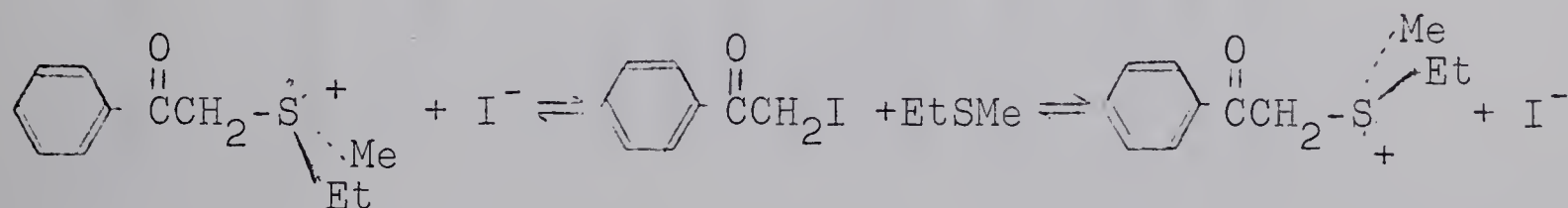








TABLE XII

RELATIVE RATES OF RACEMIZATION AND SOLVOLYSIS FOR t-BUTYLETHYLMETHYLSULFONIUM  
PERCHLORATE IN A VARIETY OF SOLVENTS

Solvent	$\mu$	50°						25°					
		rel $k_t^a$	rel $k_A^b$	rel $k_1^c$	$k_A/k_t$	rel $k_t^a$	rel $k_A^b$	rel $k_1^c$	$k_A/k_t$	rel $k_t^a$	rel $k_A^b$	rel $k_1^c$	$k_A/k_t$
EtOH	0.030	(1)	(1)	(1)	10	(1)	(1)	(1)	(1)	(1)	(1)	(1)	18
HOAc	0.042	0.80	0.93	0.95	11	0.77	0.92	0.93	0.93	0.92	0.93	0.93	21
50%AcOAc	0.042	0.58	0.99	1.0	17	0.53	0.93	0.96	0.96	0.93	0.93	0.96	31
H <sub>2</sub> O	0.030	0.36	0.64	0.67	17	0.30	0.57	0.60	0.60	0.57	0.57	0.60	33
(CH <sub>3</sub> ) <sub>2</sub> CO	0.030	1.2	1.0	1.0	8	1.2	1.0	0.95	0.95	1.0	1.0	0.95	13
HOCH <sub>2</sub> CH <sub>2</sub> OH	0.030	0.65	0.87	0.90	13	0.63	0.68	0.70	0.70	0.68	0.68	0.70	19

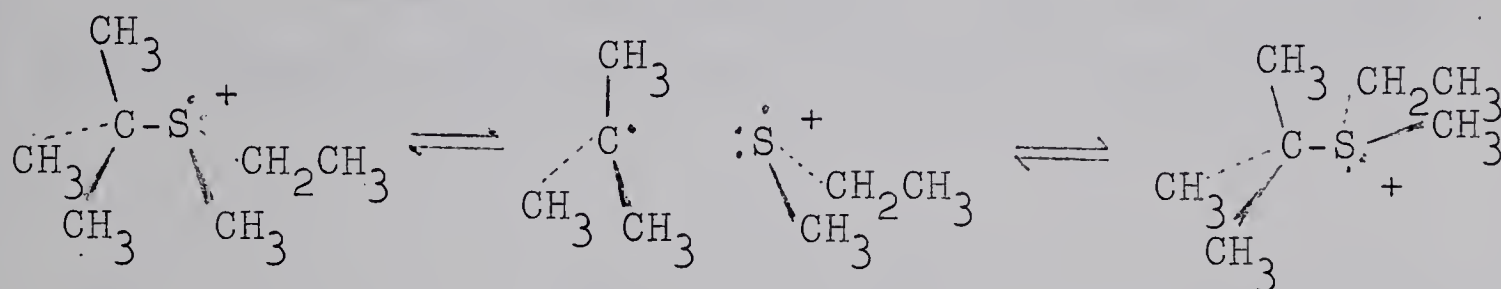
a) Titrimetric rate constant relative to the rate constant in ethanol; b) pol-  
arimetric rate constant relative to the rate constant in ethanol; c)  $k_1 = \frac{1}{2}(k_A - k_t)$ ,  
relative to  $k_1$  in ethanol; d) 0.0293 M added sodium acetate; e) 50 volume per cent  
acetic anhydride-acetic acid; f) 0.0150 M added 2,6-lutidine.



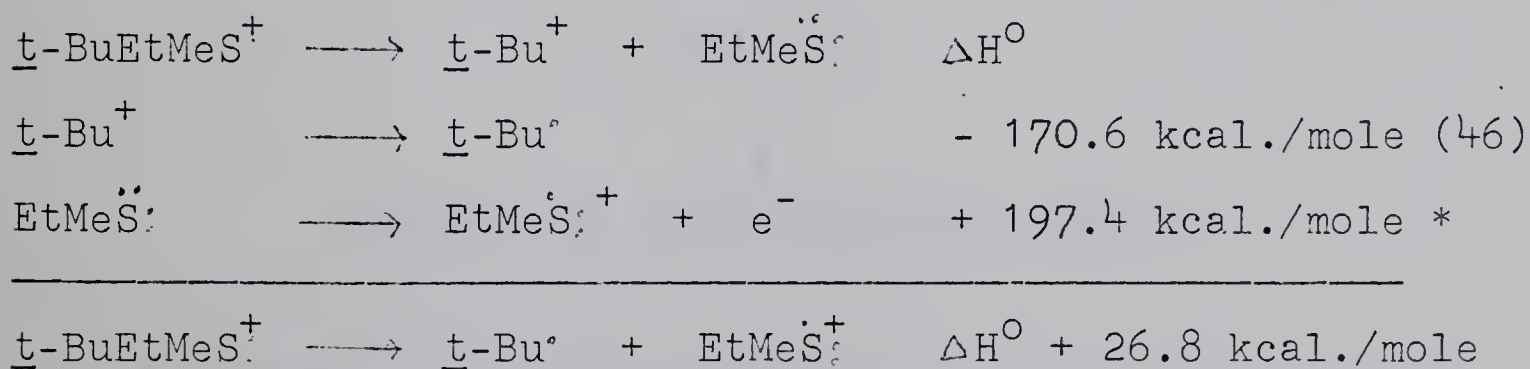
nucleophilic (45) and consequently cannot displace the sulfide group.

Racemization of sulfonium salts also cannot involve nucleophilic displacement by the solvent or its lyate anion since this reaction is not reversible under our conditions.

The possibility that racemization may occur by homolysis of the carbon-sulfur bond can be immediately discarded because (i) the formation of a t-butyl radical and an ethyl methyl sulfide ion-molecule would be energetically less



favored than the formation of a t-butyl cation and an ethyl methylsulfide molecule as shown below.

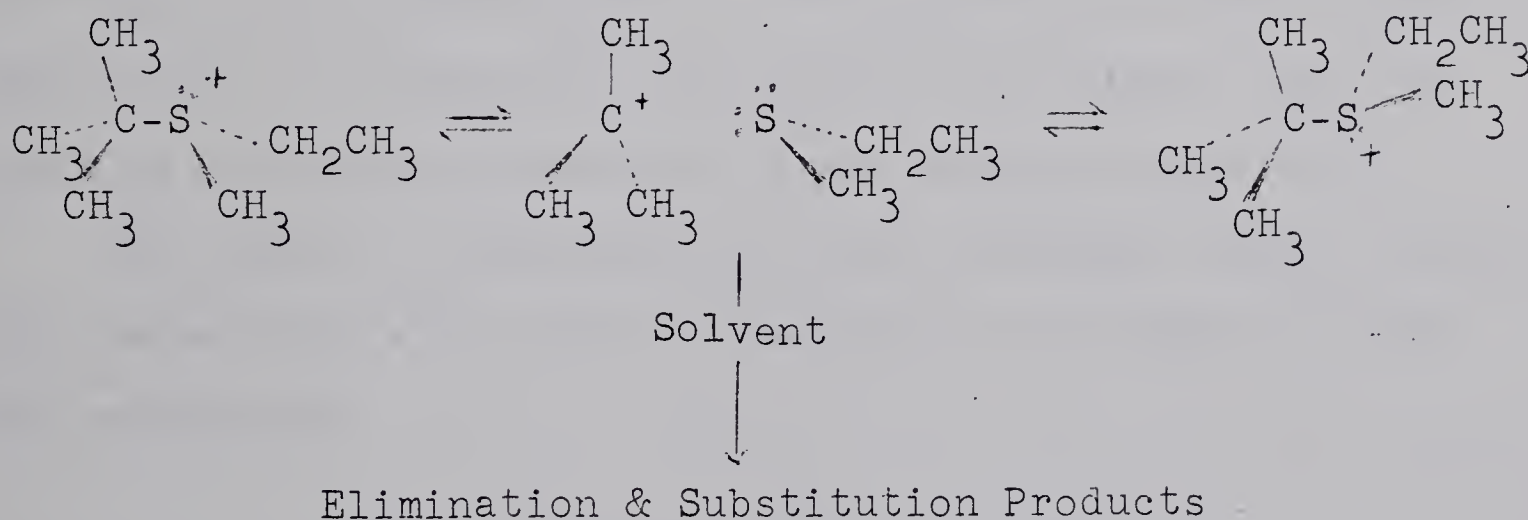


\* The heat of reaction for the ionization of ethyl methyl sulfide is the average of the ionization potentials of dimethylsulfide, 8.69 e.v., and diethyl sulfide, 8.43 e.v. (47)



Thus, for the gas-phase reaction, homolysis would require 26.8 kcal./mole more energy than heterolysis. For the reaction in solution, the effects of solvation and polarization of adjacent groups would, to a first approximation, be similar in the two processes. Hence carbon-sulfur bond homolysis can be excluded.

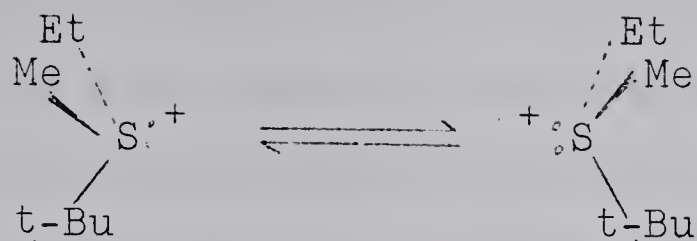
There are two possible mechanisms which can account for the racemization of t-butylethylmethylsulfonium perchlorate. (i) A heterolytic carbon-sulfur bond cleavage to form a t-butyl cation-ethyl methyl sulfide pair which can return to racemic sulfonium salt or react with solvent to form products either directly or by way of dissociated ions.



(ii) A pyramidal inversion about the central sulfur atom analogous to the inversion of an ammonia molecule.







The first mechanism represents an attractive possibility. It involves detection of an ion-neutral molecule pair during solvolysis by racemization of an optically active leaving group. Such a process has been at least formally demonstrated to occur in the diastereomer interconversion observed during the solvolysis of  $\alpha$ -phenylethyl 2,6-dimethylbenzenesulfinate in 60 per cent ethanol-water. Darwish and McLaren (27, 28) have shown that the rates of diastereomer interconversion, solvolysis and rearrangement to the sulfone all show similar sensitivity to *p*-methoxy substitution and suggest that all processes involve heterolysis of the carbon-oxygen bond.

The effect of variation of ionic strength, anion, solvent and temperature will now be considered with regard to those two mechanisms.

#### Effect of Varying of Ionic Strength

Increasing the ionic strength either by increasing the concentration of the substrate or by adding the inert salt, lithium perchlorate, has no effect on the rates of solvolysis





or racemization of t-butylethylmethylsulfonium perchlorate in anhydrous ethanol or anhydrous acetone (Tables V, VI). Hyne and Jensen (19) have reported that the rate of solvolysis of t-butyldimethylsulfonium iodide in ethanol is not affected by added lithium perchlorate or nitrate. The absence of a salt effect on the rate of racemization could be consistent with mechanism (i). It could however also be consistent with mechanism (ii). A distinction between mechanisms (i) and (ii) cannot be made on the basis of the effect of varying the ionic strength of the solution.

#### Effect of Varying the Anion

In the solvents investigated, the solvolysis of t-butylethylmethylsulfonium bromide was slightly faster than that of the corresponding sulfonium perchlorate (Tables VI, VII, IX). Swain et al. (15) observed similar small effects of the anion on the rate of hydrolysis of t-butyldimethylsulfonium salts in 90 per cent acetone-water and concluded that the anion did not appear to be involved in the mechanism of reaction. Changing the anion has very little effect on the rate of racemization. The effect of varying the anion could be consistent with the two possible mechanisms for racemization.

#### Solvent Effects



On the basis of their solvation hypothesis, Ingold et al. (9, 12) predicted a small decrease in the rate of solvolysis of t-alkyldimethylsulfonium salts as the ionizing power of the solvent is increased. In agreement with their prediction, they observed that the rate constant for solvolysis of t-butyldimethylsulfonium iodide at 50° was 2.9 times greater in ethanol than in water. t-Butylethylmethylsulfonium perchlorate exhibits a similar behavior. At 50°, the rate constant for ethanolysis is 2.7 times greater than the rate constant for hydrolysis (Tables VI, VII).

Swain et al. (15) have attempted to correlate the rates of solvolysis of t-butyldimethylsulfonium chloride to the reciprocal of the dielectric constant, the logarithm of the dielectric constant, the solvent ionizing power, the solvent nucleophilicity or electrophilicity but found that none of the correlations were very good. On the basis of dielectric constant, dipole moments or basicity, one would expect the rate to be fastest in acetic acid. In fact, the reaction in acetic acid was unusually slow. The authors associated the relatively low rate in acetic acid with the low nucleophilicity of the solvent. They postulated that the rate determining step was the reaction between acetic acid and the trimethylcarbonium ion rather than the formation of the trimethylcarbonium ion.



Solvent variation has very little effect on the rate of racemization as can be seen in Tables VI and VII. The polarimetric rate constants in ethanol, acetone and acetic acid are the same within experimental error. The rate constant in water is 40 per cent less than in ethanol.

Addition of acetic anhydride to acetic acid increases the ionizing power of the solvent without affecting its nucleophilicity. The rate of solvolysis in 50 volume per cent acetic anhydride-acetic acid is ca. 30 per cent slower than that in pure acetic acid. Addition of acetic anhydride to acetic acid has no effect on the rate of racemization.

In general, the effect of solvent variation on the rates of racemization and solvolysis of t-butylethylmethylsulfonium salts are small and could be consistent with both mechanisms (i) and (ii).

The effect of solvent viscosity on the rates of racemization and solvolysis of t-butylethylmethylsulfonium perchlorate was also examined. At 25<sup>0</sup>, ethylene glycol has a dielectric constant of 37.7, intermediate between water, 80, and ethanol, 24.3 and its viscosity is 16 times greater than that of water or ethanol (49). The relative rates of solvolysis at 50<sup>0</sup> are ethanol : ethylene glycol : water as 1 : 0.65 : 0.36; the relative rates of racemization are 1 : 0.87 : 0.64. It is evident that viscosity has little effect on either rate.





## Temperature Effects

Increasing the temperature from 25° to 50° increases the titrimetric rate for ethanolysis of t-butylethylmethylsulfonium perchlorate by a factor of 53 and increases the polarimetric rate by a factor of 31 (Table V). To determine the effect of temperature on the rates of solvolysis and racemization, the Arrhenius equation was employed:

$$k = A e^{-E_a/RT}.$$

For reactions in solution, the heat of activation (50)

$$\Delta H^\ddagger = E_a - RT = (E_a - 0.59) \text{ kcal./mole at } 25^\circ.$$

The entropy of activation,  $\Delta S^\ddagger$ , is derived from the equation (50):

$$k = k_B T/h \cdot e^{\Delta S^\ddagger/R} \cdot e^{-\Delta H^\ddagger/RT}$$

where  $k_B$  is Boltzman's constant and  $h$  is Plank's constant.

Thus at 25°,

$$\Delta S^\ddagger = 4.576(\log k_{25^\circ} - 12.79 + \Delta H^\ddagger/1.365) \text{ e.u.}$$

For racemization, the polarimetric rate constants were corrected to account for the small amount of solvolysis occurring at the same time:





$$k_1 = \frac{1}{2} (k_{\text{r}} - k_{\text{t}})$$

where  $k_1$  is the specific first-order rate constant for the conversion of one enantiomer to the other.

The values calculated for the enthalpy and entropy of activation for the racemization and solvolysis of t-butylethylmethylnsulfonium salts in various solvents are presented in Table XIII.

On the basis of their solvation theory, Ingold et al. (10) predicted that the polarity of the medium would have little effect on the activation parameters for the solvolysis of sulfonium salts which react by bond heterolysis. The heats and entropies of activation for the solvolysis of t-butylethylmethylnsulfonium perchlorate in a variety of solvents are respectively within experimental error within each other:  $\Delta H^\ddagger = 30.3 \pm 0.4$  kcal./mole and  $\Delta S^\ddagger = 14 \pm 1$  e. u. Similarly, the activation parameters for racemization are not greatly affected by changes in solvent:  $\Delta H^\ddagger = 25.7 \pm 0.6$  kcal./mole and  $\Delta S^\ddagger = 4 \pm 2$  e. u. However the heat and entropy of activation for racemization in ethylene glycol are slightly greater,  $\Delta H^\ddagger = 27.7 \pm 0.5$  kcal./mole and  $\Delta S^\ddagger = 8 \pm 1$  e. u. (Table XIII).

Changing the anion from perchlorate to bromide has no effect on the activation parameters for solvolysis but causes a small increase in the activation parameters for



TABLE XIII

ACTIVATION PARAMETERS FOR THE SOLVOLYSIS AND RACEMIZATION OF t-BUTYLETHYLMETHYLSULFONIUM SALTS IN A VARIETY OF SOLVENTS AT 25.00°.

Solvent	Anion	Solvolution		Racemization	
		$\Delta H_s^\ddagger$	$\Delta S_s^\ddagger$	$\Delta H_r^\ddagger$	$\Delta S_r^\ddagger$
EtOH	$\text{ClO}_4^-$	29.9±0.3	14±1	25.0±0.5	2±2
HOAc <sup>a</sup>	$\text{ClO}_4^-$	30.1±0.2	14±1	25.2±0.6	2±2
50%AcOAc <sup>ab</sup>	$\text{ClO}_4^-$	30.5±0.2	15±1	25.7±0.7	4±2
H <sub>2</sub> O	$\text{ClO}_4^-$	31.2±0.2	16±1	25.9±1.0	4±3
(CH <sub>3</sub> ) <sub>2</sub> CO <sup>c</sup>	$\text{ClO}_4^-$	29.8±0.5	14±2	25.6±0.5	4±2
HOCH <sub>2</sub> CH <sub>2</sub> OH	$\text{ClO}_4^-$	30.1±0.3	14±1	27.0±0.2	8±1
EtOH <sup>c</sup>	Br <sup>-</sup>	29.8±0.4	14±1	27.7±0.5	10±2
HOAc <sup>a</sup>	Br <sup>-</sup>	29.7±0.4	13±1	26.9±0.5	9±2
50%AcOAc <sup>ab</sup>	Br <sup>-</sup>	29.1±1.1	11±3	27.5±0.4	11±2

a) 0.0293 M added sodium acetate; b) 50 volume per cent acetic anhydride-acetic acid; c) 0.0510 M added 2,6-lutidine.



racemization (Table XIII).

From the Arrhenius parameters reported by Ingold and co-workers (10) for the hydrolysis of t-butyldimethylsulfonium salts,  $E_a = 33.0$  kcal./mole and  $\log A = 17.1$ , the enthalpy and entropy of activation can be calculated. They are 32.4 kcal./mole and 17.6 e. u. respectively. Recently Robertson et al. (77) reported that  $\Delta H^\ddagger = 31.56$  kcal./mole and  $\Delta S^\ddagger = 15.74$  e. u. for the hydrolysis of t-butyldimethylsulfonium chloride. Although these values are probably within experimental error from the corresponding values observed for the hydrolysis of t-butylethylmethylsulfonium perchlorate, 32.4 kcal./mole and 16 e. u., it is interesting to note that substituting one of the methyl groups in t-butyldimethylsulfonium salts by an ethyl group should increase the energy of the ground state relative to the transition state due to non-bonded interactions, thereby causing a small decrease in the heat of activation.

A distinction between the two mechanisms cannot be made on the basis of the evidence presented so far. In Chapter II, substituent effects will be examined in order to differentiate which mechanism controls the racemization of t-butylethylmethylsulfonium salts.





## EXPERIMENTAL

### PHYSICAL MEASUREMENTS

All melting points were obtained using a Hershberg type melting point apparatus with a set of Anschutz thermometers. All values are uncorrected.

Refractive indices were obtained on a Bausch and Lomb Abbe 3L Refractometer thermostated at 25.0°.

Nuclear magnetic resonance spectra were recorded on a Varian Analytical Spectrophotometer Model A-60.

Infrared spectra were recorded on a Perkin-Elmer Recording Infrared Spectrophotometer Model 421.

Ultraviolet and visible spectra were obtained on a Perkin-Elmer Ultraviolet-visible Spectrophotometer Model 202.

Optical rotation measurements were obtained on a Perkin-Elmer Polarimeter Model 141. Kinetic analyses were done with incident light having a wavelength of 436 mμ.

Gas chromatographic analyses were made on a Perkin-Elmer Model 154D Vapor Fractometer modified with a high temperature filament detector 154-0370 and a Honeywell Disc Chart Integrator Model 201 B.

Elemental analyses were performed by Mrs. D. Mahlow.

### SOLVENTS





### Anhydrous Ethanol

Anhydrous ethanol was prepared from commercially available 95% ethanol by initial dehydration with calcium oxide followed by treatment with magnesium ethoxide as described by Fieser (51). A Karl Fischer titration was done to verify that the solvent was anhydrous (52).

### Anhydrous Acetic Acid

Baker and Adamson reagent grade glacial acetic acid was purified by a procedure described by Fainberg and Winstein (48). The amount of water present was determined by Karl Fischer titrations and an equivalent amount of acetic anhydride was added to the solvent. The mixture was refluxed for 24 hours and fractionally distilled. The water content of the distillate was determined and sufficient acetic anhydride was added to neutralize any water present and leave a 0.1 molar excess of acetic anhydride in the solution. The solution was refluxed for 12 hours but not distilled.

### Acetic Anhydride

Fisher certified reagent acetic anhydride was distilled through a 70 cm. Vigreux column. The forerun, (25 per cent of the total distillate) was discarded and the middle cut was used without further treatment. 50% AcOAc indicates 50 volume per cent acetic anhydride in acetic acid.

### Anhydrous Acetone

Shawinigan reagent grade acetone was allowed to perco-



late through a 60 cm. column packed with Linde type 4A molecular sieves. A small amount of molecular sieves was added to the eluate before it was distilled through a 70 cm. Vigreux column. The water content of the acetone was determined by a Karl Fisher titration using anhydrous pyridine as the solvent as suggested by Smith, Fainberg and Winstein (53). The purified acetone was not stored, but rather a fresh batch was prepared each time the solvent was required.

#### Ethylene Glycol

Fisher certified ethylene glycol was purified and dried using molecular sieves as described above. A Karl Fischer titration of the solvent prior to any use ascertained its anhydrous nature (52).

#### REAGENTS AND MATERIALS

##### 2,6-Lutidine

Eastman practical grade 2,6-lutidine was dried over potassium hydroxide for several days, followed by refluxing and distillation from barium oxide as described by Fieser for the preparation of anhydrous pyridine (54). The center cut was treated with boron trifluoride as described by Brown et al. (55). B.p.  $140^{\circ}$  at 700 mm.,  $n_D^{25}$  1.4954 (reported (55): b.p.  $143^{\circ}$  at 760 mm.,  $n_D^{25}$  1.4953).



### Pyridine

Eastman white label pyridine was stored over potassium hydroxide in a dark bottle.

### Lithium Perchlorate

Fisher certified lithium perchlorate was recrystallized from water to yield the trihydrate, m.p.  $94.6-95.3^{\circ}$  (reported (56):  $93-94.5^{\circ}$ ). The trihydrate was quantitatively dehydrated as described by Winstein and Adams (56).

### Standard Sodium Methoxide Solution for Titrations

A solution of sodium methoxide in methanol was prepared by the addition of a weighed amount of freshly cleaned sodium to one gallon of Fisher certified anhydrous methanol. The resulting solution was standardized with Fisher certified primary standard potassium hydrogen phthalate in water using phenolphthalein as indicator. Restandardization showed the solution to stable for at least two years when it is stored in a tightly stoppered dark bottle.

### Standard Sodium Acetate Solution for Titrations

Baker and Adamson reagent grade sodium carbonate was dried to constant weight in a sand bath at  $250^{\circ}$  as described by Kolthoff and Sandel (57). A standard solution of sodium acetate in acetic acid was prepared by placing an accurately weighed portion of dried sodium carbonate in a 1000 ml. volumetric flask and adding Baker and Adamson reagent grade glacial acetic acid to the mark (58).







### Sodium Acetate Solution in Anhydrous Acetic Acid

A stock solution of sodium acetate in anhydrous acetic acid was prepared in the same manner as described above.

### Standard Perchloric Acid Solution for Titrations

A measured quantity of Baker and Adamson reagent grade 70 per cent perchloric acid was added to glacial acetic acid. This solution was standardized with standard sodium acetate solution using *p*-naphtholbenzein in glacial acetic acid as indicator (44).

### *t*-Butyl Ethyl Sulfide

A 400 g. quantity of 75 weight per cent sulfuric acid (170 ml. of concentrated sulfuric acid and 100 ml. of water) was placed into a two-liter three-neck flask equipped with a stirrer, a dropping funnel and a condenser. The temperature was maintained at 0° by an ice-water bath. *t*-Butyl alcohol (60 g., 0.8 mole) and ethyl mercaptan (25 g., 0.4 mole) were successively added dropwise into the flask. After the addition was complete, the cooling bath was removed and stirring was continued for two hours. Crushed ice (ca. 1000 g.) was added to the solution and the mixture was extracted three times with 200 ml. portions of ethyl ether in a three-liter separatory funnel. The combined ethereal portions were washed with water, a 10 per cent sodium hydroxide solution and three more times with water. The ether solution was dried over anhydrous potassium carbonate and fractionally distilled through a 40 cm.



Vigreux column. Yield 42 g. (88 per cent), b.p. 116.5-117.8° at 712 mm.,  $n_D^{25}$  1.4405 (reported: (59) b.p. 120.4°,  $n_D^{25}$  1.4390; (60) b.p. 119.5° at 761 mm.,  $n_D^{20}$  1.44164). N.m.r. (CDCl<sub>3</sub>):  $\tau$  8.77 (t, J=7.5 cps., 3 H), 8.68 (s, 9 H), 7.44 (q, J=7.5 cps., 2 H). Ultraviolet (ethanol):  $\lambda_{\max}$  216 m $\mu$  (log  $\epsilon$  2.98).

Anal. Calcd. for C<sub>6</sub>H<sub>14</sub>S: C, 60.95; H, 11.93.

Found: C, 60.63, 61.15; H, 11.86, 11.90.

t-Butylethylmethylsulfonium Iodide

Nitromethane (300 ml.) was added to an excess of t-butyl ethyl sulfide (172 g., 1.5 moles) in iodomethane (200 g., 1.4 moles). The mixture was allowed to stand in the dark at room temperature for two hours, then was kept in the freezer compartment of the refrigerator for one day. The precipitate was filtered and washed with ethyl ether. The white crystals turn yellowish-brown when exposed to heat and/or light. The iodide was recrystallized from a methanol-ethyl ether solution. Yield 230 g. (62 per cent), m.p. 135° (dec.). N.m.r. (CDCl<sub>3</sub>):  $\tau$  8.38 (t, J=7.5 cps., 3 H), 8.24 (s, 9 H), 6.82 (s, 3 H), 6.32 (q, J=7.5 cps., 2 H).

Anal. Calcd. for C<sub>7</sub>H<sub>17</sub>IS: C, 32.31; H, 6.59.

Found: C, 32.44, 32.64; H, 6.36, 6.30.

(-)-2R,3R-Dibenzoyltartaric Acid Monohydrate

(-)-2R,3R-Dibenzoyltartaric acid monohydrate was prepared from 200 g. (1.3 moles) of (+)-2R,3R-tartaric acid



as described by Butler (61). Yield 39<sup>4</sup> g. (78 per cent), m.p. 88-89°, (reported: (61) 88-89°, (62) 88-90°).  $[\alpha]_D^{25}$  -116 (c 0.298, methanol); reported: (61)  $[\alpha]_D^{25}$  -116.0, (62)  $[\alpha]_D^{18}$  -115.78, (63)  $[\alpha]_D^{25}$  -114.8. N.m.r. (CDCl<sub>3</sub>):  $\tau$  4.07 (s, 2 H). 2.8-2.4 (m, 6 H), 2.2-1.8 (m, 4 H), 1.17 (s, 4 H). Infrared: 3600-2500, 1738, 1604, 1586, 1493, 1450, 1260, 1115, 880, 727 and 706 cm.<sup>-1</sup>. Ultraviolet (ethanol):  $\lambda_{\max}$  230 m $\mu$  (log $\epsilon$  4.40).

Neut. equiv. Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>9</sub>: 188.2. Found: 190.

Anal. Calcd. for C<sub>18</sub>H<sub>16</sub>O<sub>9</sub>: C, 57.45; H, 4.29.

Found: C, 57.38, 57.53; H, 4.22, 4.63.

(-)-t-Butylethylmethylsulfonium 2R,3R-Dibenzoylhydrogentartrate

t-Butylethylmethylsulfonium iodide (59.0 g., 0.23 mole), dissolved in 100 ml. of 90 per cent methanol-water, was percolated through a 60 cm. Dowex 1 x8 anion exchange resin column, which had previously been converted to its hydroxide form by passing a 5 per cent sodium hydroxide solution through the column until the eluate no longer gave a precipitate with an acidic silver nitrate solution. The rate of elution was approximately 100 ml. per hour. The presence of the sulfonium hydroxide in the eluate was determined by sampling aliquots with phenolphthalein. Elution with 90 per cent methanol-water was continued until the test was neutral. The eluate was also tested after each 50 ml. cut to certify that iodide ions were absent. The sulfonium hydroxide was neutralized by collecting the eluate in a





flask containing an excess of (-)-2R,3R-dibenzoyltartaric acid monohydrate dissolved in ethyl ether. The solvent was removed using a rotary evaporator and the white solid was triturated several times with ethyl ether in order to remove any excess dibenzoyltartaric acid.

t-Butylethylmethylsulfonium 2R,3R-dibenzoylhydrogen-tartrate was recrystallized by dissolving the racemic salt into 90 per cent methanol-water, adding an equal volume of ethyl ether and setting the solution in the freezer for several days. Resolution was achieved by recrystallizing the salt until a constant specific rotation was obtained (usually three or four times). The mother liquor was also kept for further treatment. Yield 29.0 g. (52 per cent), m.p. 112.6° (dec.),  $[\alpha]_D^{25} -106$ , ( $c$  1.60, methanol). Ultra-violet (ethanol):  $\lambda_{max}$  235 m $\mu$  (log  $\epsilon$  4.26). N.m.r. (dimethylsulfoxide- $d_6$ ):  $\tau$  8.64 (t,  $J=7.5$  cps., 3 H), 8.52 (s, 9 H), 7.17 (s, 3 H), 6.78 (q,  $J=7.5$  cps., 2 H), 4.36 (s, 2 H), 2.6-2.3 (m, 6 H), 2.2-1.9 (m, 4 H). Infrared: 3085, 3060, 3030, 1738, 1705, 1670, 1605, 1587, 1494, 1450, 1410, 1260, 1160, 1115, 732 and 710  $cm^{-1}$ .

Neut. equiv. Calcd. for  $C_{25}H_{30}O_8S$ : 490.6. Found: 490.

Anal. Calcd. for  $C_{25}H_{30}O_8S$ : C, 61.21; H, 6.16; S, 6.54.

Found: C, 61.10, 60.94, 60.87; H, 6.52, 6.47, 6.44;  
S, 6.59, 6.35.

#### dl-t-Butylethylmethylsulfonium Perchlorate

A 10.4 g. (0.04 mole) quantity of t-butylethylmethylyl-





sulfonium iodide dissolved in 25 ml. of 90 per cent methanol-water was passed through a Dowex 1 x8 anion exchange resin column in its hydroxide form as described above. The sulfonium hydroxide eluted was immediately neutralized with a 5 per cent perchloric acid solution and the solvent was quickly removed in a rotary evaporator. Caution, since concentrated perchloric acid may be explosive in the presence of organic materials, care must be taken that the pH is never lower than 7 when the last traces of solvent are removed. The white solid was recrystallized from a cold methanol-ether solution. Yield 6.6 g. (71 per cent), m.p.  $148^{\circ}$  (dec.). N.m.r. (dimethylsulfoxide- $d_6$ ):  $\tau$  8.60 (t,  $J=7.5$  cps., 3 H), 8.49 (s, 9 H), 7.16 (s, 3 H), 6.78 (q,  $J=7.5$  cps., 2 H). Infrared: 1086, 627 and 607  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_7\text{H}_{17}\text{ClO}_4\text{S}$ : C, 36.12; H, 7.36; S, 13.78.

Found: C, 36.37, 35.88; H, 7.20, 7.01; S, 13.67, 13.97.

(-)-t-Butylethylmethylsulfonium Perchlorate

(-)-t-Butylethylmethylsulfonium 2R,3R-dibenzoylhydrogen-tartrate (3.3 g., 0.007 mole) was dissolved in 30 ml. of 90 per cent methanol-water containing an equimolar amount of perchloric acid. An equal volume of ethyl ether was added to the solution and the mixture was placed in freezer for several days. The precipitate was triturated several times with a 1:1 mixture of acetone-ethyl ether and recrystallized from a cold solution of methanol-ethyl ether. The optically active salt can also be prepared with an anion exchange resin



as described for the racemate. Yield 1.0 g. (60 per cent), m.p.  $148.6^{\circ}$  (dec.).  $[\alpha]_D^{25} -34.6$  ( $c$  1.51, methanol),  $[\alpha]_{436}^{25} -65.5$  ( $c$  0.468, methanol). The salt did not lose any optical activity over a period of two years when stored in a tightly stoppered flask kept in the freezer compartment of the refrigerator. N.m.r. and infrared spectra were superimposable upon those of the corresponding racemic salts. Anal. Calcd. for  $C_7H_{17}ClO_4S$ : C, 36.12; H, 7.36.

Found: C, 36.44, 35.95, 36.24; H, 7.27, 7.31, 7.39.

(+)-t-Butylethylmethylsulfonium Perchlorate

An excess of perchloric acid was added to the mother liquors obtained from the resolution of t-butylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartrate. Ethyl ether was added until the solution became turbid and the mixture was placed in the freezer for several days. The dextrorotary perchlorate salt was obtained and purified in the same manner as its enantiomer. Yield 5.7 g. (13 per cent), m.p.  $149^{\circ}$  (dec.).  $[\alpha]_D^{25} +27.5$  ( $c$  3.66, methanol). N.m.r. and infrared spectra were superimposable upon that of the racemic and (-)-t-butylethylmethylsulfonium perchlorates. This and the fact that the rates of solvolysis and racemization of these isomers are identical unequivocally establishes that the sulfonium 2R,3R-dibenzoylhydrogentartrate was at least partially separated into its diastereomers.

Anal. Calcd. for  $C_7H_{17}ClO_4S$ : C, 36.12; H, 7.36.

Found: C, 36.13, 36.55; H, 7.15, 7.39.



dl-t-Butylethylmethylsulfonium Bromide

t-Butylethylmethylsulfonium iodide (18.0 g., 0.07 mole), dissolved in 100 ml. of 90 per cent methanol-water was passed through a Dowex 1 x8 anion exchange resin, in its hydroxide form, as described for the preparation of the perchlorate salt. The eluate was neutralized with hydrobromic acid and the solvent removed in a rotary evaporator. The bromide salt was recrystallized from nitromethane-ethyl ether at low temperature. Yield 8.3 g. (56 per cent), m.p.  $121^{\circ}$  (dec.). N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  8.38 (t,  $J=7.5$  cps., 3 H), 8.30 (s, 9 H), 6.82 (s, 3 H), 6.36 (q,  $J=7.5$  cps., 2 H).

(-)-t-Butylethylmethylsulfonium Bromide

A 4.9 g. (0.01 mole) quantity of (-)-t-butylethylmethylsulfonium 2R,3R-dibenzoylhydrogen tartrate, dissolved in 80 ml. of 90 per cent methanol-water, was passed through a Dowex 1 x8 anion exchange resin in its hydroxide form as described previously. To minimize racemization during exchange, the jacketed column was maintained at  $0^{\circ}$  by circulating water from an ice-water bath through the jacket. Previous tests had shown that the selectivity of the resin towards dibenzoylhydrogentartrate anion was much greater than that toward hydroxide anion, so that elution can be carried out at a rate of 250 ml. per hour without danger of breakthrough. Since the color of the resin in the dibenzoylhydrogentartrate form is lighter than that of the hydroxide form exchange is readily observed. The eluate







was treated in the same manner as the corresponding racemate. Yield 1.9 g. (90 per cent), m.p.  $120^{\circ}$  (dec.).

$[\alpha]_D^{25}$  -27.3,  $[\alpha]_{436}^{25}$  -57.9 ( $c$  0.243, ethanol). N.m.r.

and infrared spectra were identical with those of the racemate.

Absence of the carbonyl band in the infrared spectrum confirmed the completeness of exchange.

Anal. Calcd. for  $C_7H_{17}BrS$ : C, 39.44; H, 8.04.

Found: C, 39.37, 39.20; H, 7.84, 7.94.

#### Racemization of (-)-t-Butylethylmethysulfonium Perchlorate

##### Run 1-97

A solution of 0.139 g. of t-butylethylmethysulfonium perchlorate in 25 ml. of anhydrous ethanol having a rotation of  $[\alpha]_D^{25}$  of  $-0.134 \pm 0.012^{\circ}$  (Rudolph Polarimeter Model 80, 4 dm. polarimeter tube) was placed in a  $25^{\circ}$  constant temperature bath for 55 hours. The optical rotation had decreased to  $-0.002 \pm 0.008$ . A 50 ml. quantity of ethyl ether was added to the solution and the mixture was placed in the freezer. The white precipitate was filtered and dried. Yield 0.07 g. (50 per cent). Melting point, n.m.r. and infrared spectra indicated that the recovered material was racemic t-butylethylmethysulfonium perchlorate.

#### KINETICS

##### Titrimetric Rates

The sulfonium salt was accurately weighed in a tared



volumetric flask. Enough solvent to dissolve the salt, together with as many aliquots of a standard solution of base or inert salt as required, was added to the flask. After dilution to the mark, the solution was equilibrated by shaking the flask 100 times.

For reactions at  $50^{\circ}$  and  $70^{\circ}$  the sealed ampoule technique was employed. Aliquots of the solution (5.3 ml.) were transferred to partially drawn out test tubes which had previously soaked overnight in a hot soap solution, rinsed eight times with distilled water and dried overnight in an oven at  $120^{\circ}$ . The test tubes were sealed and placed in a constant temperature bath,  $50.00 \pm 0.02$  or  $70.00 \pm 0.02^{\circ}$ . At appropriate time intervals the ampoules were removed from the bath, placed in an ice-acetone bath and shaken for 30 seconds in order to quench the reaction. The first point was taken at least 4 minutes after the ampoules were placed in the bath so as to ensure temperature equilibration. Infinity measurements were taken at approximately 10 and 20 half-lives. Before the ampoules were broken open, they were allowed to equilibrate to  $25^{\circ}$  in a constant temperature bath for 5 minutes. A 5 ml. aliquot was removed by means of a calibrated automatic pipette and delivered into a 50 ml. Erlenmeyer flask containing 25 ml. of boiled distilled water. Each sample was titrated for developing acid with a standard solution of sodium methoxide in methanol using phenolphthalein as



indicator.

For reactions at  $25^{\circ}$ , the sealed ampoules were removed from the constant temperature bath ( $25.00 \pm 0.02^{\circ}$ ) and immediately broken open without quenching the reaction. An accurately known aliquot was titrated as above. The time recorded was that at the beginning of the titration. Since the half-lives of the reactions studied varied between 30 and 400 hours, small differences in titration times were not serious.

The procedure for rates measured in acetic acid and acetic anhydride-acetic acid mixture was modified as follows. The reaction solution contained an excess of sodium acetate, prepared by adding an accurately weighed amount of constant weight sodium carbonate to anhydrous acetic acid as described previously. Each aliquot was titrated for excess base with a standard solution of perchloric acid in glacial acetic acid using a 0.1 per cent glacial acetic acid solution of p-naphtholbenzein as indicator.

The rate constants calculated are based on the experimental infinity values, usually  $100 \pm 3$  per cent, thus measure the total rate of reaction. The rates were followed to ca. 85 per cent completion. Prior to each run a minimum of 4 blanks were titrated. The blanks consist of an equal amount of solvent containing inert salt and/or base but not the reacting substrate. Percentage infinity values were





obtained from the following relationship:

$$\text{Per cent infinity titer} = \frac{V_{\infty} - V_B}{\text{Theoretical infinity titer}} \times 100$$

where  $V_{\infty}$  is the experimental infinity titer and  $V_B$  is the average titer of the blanks.

### Polarimetric Rates

Method I. Aliquots of standard solution of the optically active sulfonium salt were transferred to ampoules. The ampoules were sealed and placed in a constant temperature bath as described for the titrimetric rate analyses. Reactions measured at  $50^{\circ}$  were quenched as described above. After equilibration to  $25^{\circ}$ , the ampoules were broken open and an aliquot of the solution was transferred to a 1 dm. polarimeter tube. The optical rotation was obtained from the digital readout of a Model 141 Perkin-Elmer Polarimeter. Measurements were made using an incident light beam having a wavelength of 436 mμ. A "zero" reading was obtained before and after each measurement.

Method II. For most of the polarimetric analyses, the Model 141 Perkin-Elmer Polarimeter was equipped with a Honeywell recorder having a chart speed of 4 inches per hour. Water from a constant temperature bath,  $49.99 \pm 0.02$  or  $25.01 \pm 0.02^{\circ}$ , was circulated through jacketed polarimeter tubes. An aliquot of the solution of the optically active salt was placed in the polarimeter tube and the optical





rotation was continuously recorded. A "zero" reading was taken before and after each run. For reactions with a half-life of 30 minutes or less, the chart speed was too slow for accurate determinations. Consequently the optical rotation was taken from the digital readout at appropriate time intervals and recorded in the laboratory book.

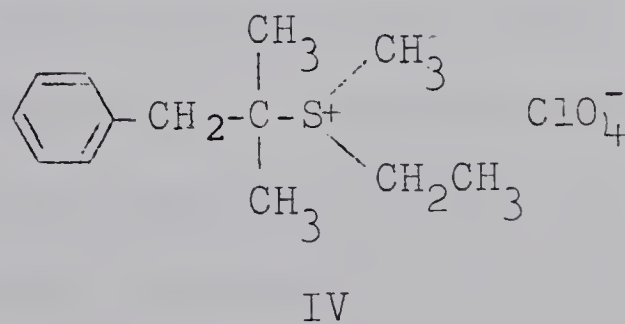
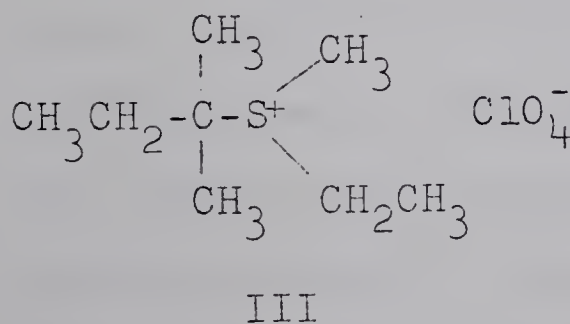
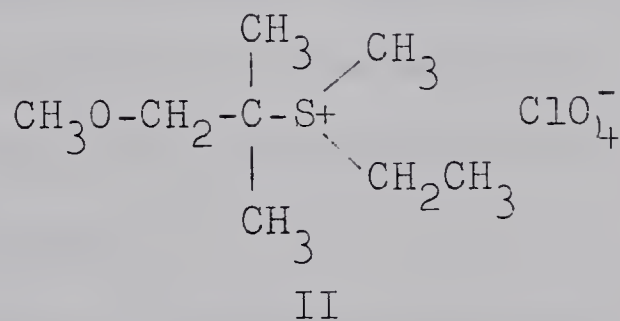
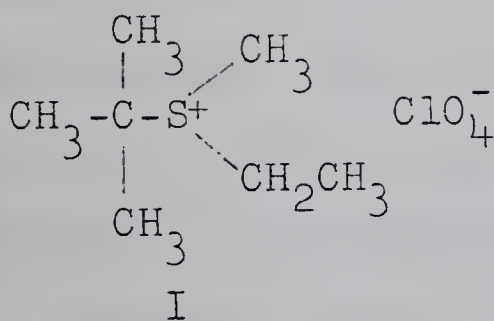
The rate constants were calculated on the basis of the experimental infinity obtained after 10 half-lives (zero). Typical rate analyses have been presented in the Result section.



## CHAPTER II

### SUBSTITUENT EFFECTS

To gain further insight into the mechanism for the racemization of *t*-butylethylmethylsulfonium salts, a study of substituent effects was undertaken. The following sulfonium salts were synthesized and resolved into their optically active isomers, 1-methoxy-2-methyl-2-propylethylmethylsulfonium perchlorate (II), *t*-amylethylmethylsulfonium perchlorate (III), and 1-phenyl-2-methyl-2-propylethylmethylsulfonium perchlorate (IV). The rates of racemization and solvolysis in various solvents will be discussed in relation to the parent *t*-butylethylmethylsulfonium perchlorate (I).





## SYNTHESIS

### 1-Methoxy-2-methyl-2-Propylethylmethylsulfonium Perchlorate, II

The route illustrated in Figure XI was followed for the preparation of 1-methoxy-2-methyl-2-propyl ethyl sulfide. Bromination of isobutyraldehyde was conducted in refluxing carbon disulfide in the presence of a molar excess of calcium carbonate to neutralize the hydrogen bromide as it is formed and thus prevent acid-catalyzed polymerization (64). The  $\alpha$ -bromoisobutyraldehyde was treated with sodium ethylmercaptide in methanol to yield  $\alpha$ -ethylmercaptoisobutyraldehyde. The aldehyde was reduced with lithium aluminum hydride yielding upon workup the corresponding alcohol. The sodium salt of this alcohol was treated with iodomethane to produce the methyl ether. A 28 per cent overall yield of 1-methoxy-2-methyl-2-propyl ethyl sulfide was obtained. Details of the synthesis and characterization of the above liquids and their solid derivatives are described in the Experimental section.

From this point, the synthesis of 1-methoxy-2-methyl-2-propylethylmethylsulfonium salts was conducted in a manner similar to that of the parent t-butylethylmethylsulfonium salts summarized in Figure III. Treatment of the sulfide with iodomethane in nitromethane yielded the sulfonium iodide. Other salts were obtained by the con-





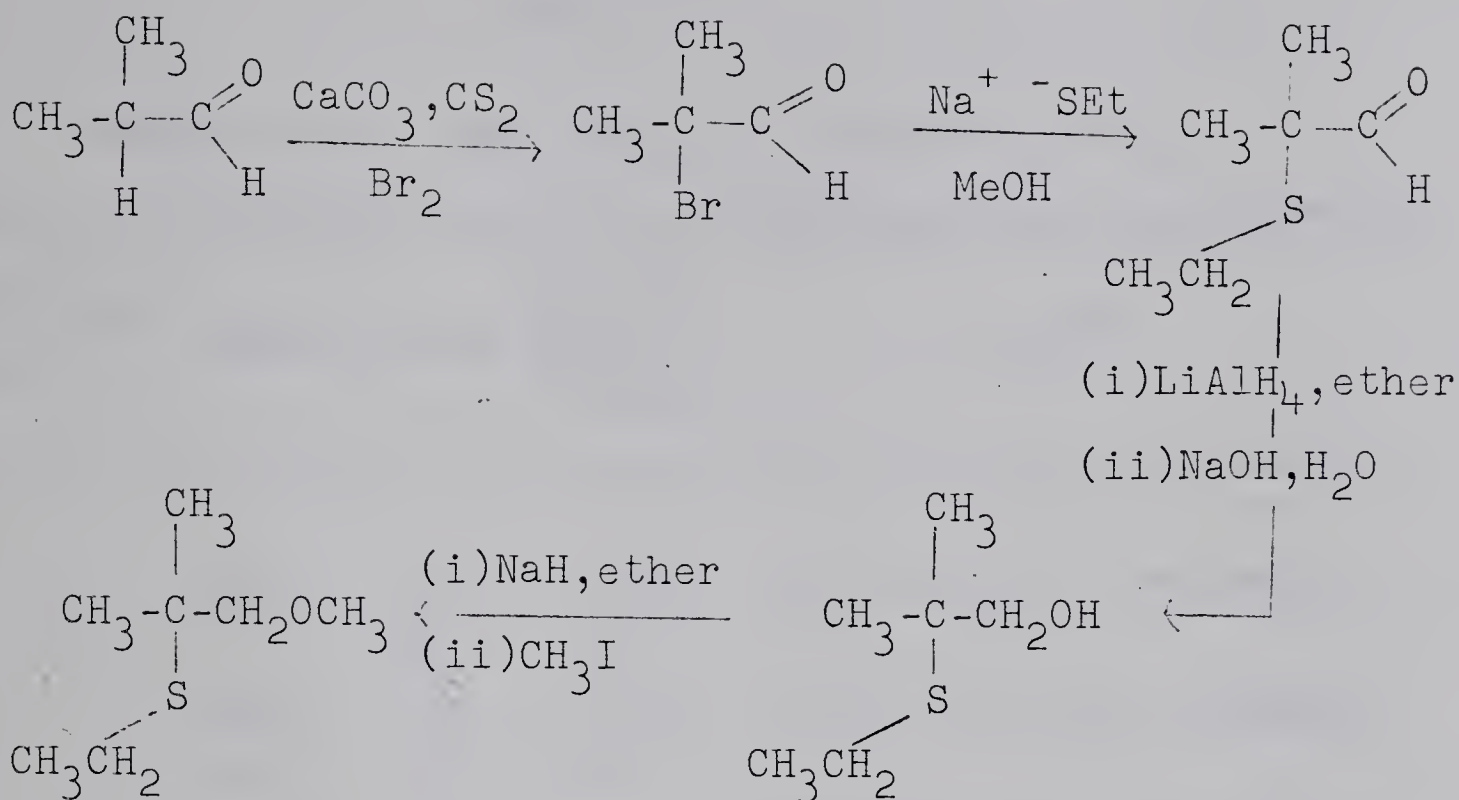


Figure XI. Synthesis of 1-methoxy-2-methyl-2-propyl ethyl sulfide.

version of the iodide into the hydroxide using a Dowex 1 x8 anion exchange resin, in its hydroxide form, followed by neutralization of the sulfonium hydroxide with the appropriate acid. The optically active perchlorate was obtained by resolution of the 2R,3R-dibenzoylhydrogen-tartrate followed by replacement of the dibenzoylhydrogen-tartrate anion by perchlorate. The overall yield based on isobutyraldehyde was 4 per cent. Details of the procedure are presented in the Experimental section and some of the properties of the sulfonium salts are listed in Table XIV.



TABLE XIV

PROPERTIES OF SOME TERTIARY SULFONIUM SALTS

Sulfonium Cation	Anion	Isomer	Melting Point (decomp.)	$[\alpha]_D^{25^\circ}$
I	$\text{ClO}_4^-$	(-)	148.6	-34.6 ( $\underline{c}$ 1.51, methanol)
II	$\text{I}^-$	dl	77	
	$\text{dBHT}^-$	(-)	122.4	-100 ( $\underline{c}$ 0.645, methanol)
	$\text{ClO}_4^-$	dl	103	
	$\text{ClO}_4^-$	(-)	102	-13.5 ( $\underline{c}$ 0.64, ethanol)
III	$\text{I}^-$	dl	101	
	$\text{dBHT}^-$	(-)	110	-104 ( $\underline{c}$ 0.628, methanol)
	$\text{ClO}_4^-$	dl	135	
	$\text{ClO}_4^-$	(-)	137	-25.1 ( $\underline{c}$ 0.43, methanol)
	$\text{ClO}_4^-$	(+)	137	+15.7 ( $\underline{c}$ 0.42, methanol)
IV	$\text{I}^-$	dl	114	
	$\text{dBHT}^-$	(-)	98	-82.6 ( $\underline{c}$ 0.560, methanol)
	$\text{ClO}_4^-$	dl	104	
	$\text{ClO}_4^-$	(-)	106	-11.0 ( $\underline{c}$ 0.53, methanol)

I t-Butylethylmethylsulfonium  
 II 1-Methoxy-2-methyl-2-propylethylmethylsulfonium  
 III t-Amylethylmethylsulfonium  
 IV 1-Phenyl-2-methyl-2-propylethylmethylsulfonium  
 dBHT<sup>-</sup> 2R,3R-Dibenzoylhydrogentartrate.



t-Amylethylmethethylsulfonium Perchlorate, III, and 1-Phenyl-2-methyl-2-propylethylmethethylsulfonium Perchlorate, IV.

These salts were prepared from t-amyl alcohol and 1-phenyl-2-methyl-2-propanol respectively by a method similar to the synthesis of t-butylethylmethethylsulfonium perchlorate described in Chapter I and illustrated in the reaction scheme in Figure III. The resolved dibenzoylhydrogentartrate salts were converted to the corresponding hydroxides using a Dowex 1 x8 anion exchange resin, in its hydroxide form, maintained at ice-water temperature. The hydroxides were neutralized with perchloric acid. A 23 per cent overall yield of (-)-t-amylethylmethethylsulfonium perchlorate and a 21 per cent yield of (-)-1-phenyl-2-methyl-2-propylethylmethethylsulfonium perchlorate were obtained (based on the starting alcohol). The optical purity of I, II, III or IV is unknown. Details and modifications of the general synthesis as well as the characteristics of all compounds are to be found in the Experimental section. Some of the properties of these sulfonium salts are listed in Table XIV.

## RESULTS

The rates of racemization and solvolysis of II, III and IV were measured in a variety of solvents in the same manner as was employed for t-butylethylmethethylsulfonium salts described in Chapter I. All rates were followed to ca. 85 per cent completion. Good straight lines were





obtained when  $\log (V_{\infty} - V_t)$  or  $\log (\alpha_{\infty} - \alpha_t)$  was plotted vs time. The results are summarized in Tables XV, XVI, and XVII. The specific first-order rate constants for the conversion of one enantiomer to the other,  $k_1$ , are also presented in these Tables.

1-Methoxy-2-methyl-2-propylethylmethylsulfonium Perchlorate, II.

The rate of solvolysis of II in ethanol at  $50^{\circ}$  has a half-life of 3 days whereas the polarimetric rate has a half-life of 14 minutes. The rate constants for solvolysis at  $25^{\circ}$  in various solvents were obtained from the values measured at  $70^{\circ}$  and  $50^{\circ}$  by extrapolation from the Arrhenius relationship. The extrapolated value for solvolysis in ethanol was the same as that obtained experimentally (Run 2-173, Table XV).

An experiment was carried out to show that the loss of optical activity was due to racemization of the substrate (Run 3-166). The melting point, n.m.r. and infrared spectra of the material recovered after the optical activity of II in ethanol had decreased to zero indicated that it was racemic 1-methoxy-2-methyl-2-propylethylmethylsulfonium perchlorate. Hence loss of optical activity arises only by racemization and solvolysis.

As with compound I, solvent has little effect on the





TABLE XV

SOLVOLYSIS OF 1-METHOXY-2-METHYL-2-PROPYLETHYLMETHYLSULFONIUM  
PERCHLORATE

Run	Solvent	Temp.	Isomer	Conc. (M)	$\mu$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_x^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )
2-165	EtOH	70	d1	0.01178	0.015	48.1± 2.1		
3-41	HOAc <sup>d</sup>	70	d1	0.01500	0.042	35.9± 0.5		
3-45	50%AcOAc <sup>de</sup>	70	d1	0.01507	0.042	25.7± 0.4		
3-115	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	70	d1	0.01193	0.015	47.4± 2.4		
2-166	EtOH	50	d1	0.01178	0.015	2.72±0.08		
2-125	EtOH	50	(-)	0.01176	0.015	2.74±0.03	805 ± 48	401 ± 24
3-43	HOAc <sup>d</sup>	50	d1	0.01500	0.042	1.87±0.13		
3-151	HOAc <sup>d</sup>	50	(-)	0.01511	0.042		870 ± 14	434 ± 7
3-47	50%AcOAc <sup>de</sup>	50	d1	0.01507	0.042	1.33±0.06		
3-147	50%AcOAc <sup>de</sup>	50	(-)	0.01513	0.042		840 ± 16	419 ± 8
3-117	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	50	d1	0.01193	0.015	2.48±0.07		
3-163	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	50	(-)	0.01216	0.015		883 ± 14	440 ± 7
2-173	EtOH	25	d1	0.01178	0.015	0.0436±0.002		
2-127	EtOH	25	(-)	0.01176	0.015	0.0436 <sup>g</sup>	27.0±1.1	13.5±0.6
3-153	HOAc <sup>d</sup>	25	(-)	0.01511	0.042	0.0266 <sup>g</sup>	26.1±0.7	13.0±0.4
3-149	50%AcOAc <sup>de</sup>	25	(-)	0.01513	0.042	0.0188 <sup>g</sup>	22.0±0.8	11.0±0.4
3-165	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	25	(-)	0.01216	0.015	0.0355 <sup>g</sup>	27.9±0.7	13.9±0.4

a) Titrimetric rate constant; b) polarimetric rate constant, rates in ethanol were done by Method I, all others by Method II (see Experimental section); c)  $k_1 = \frac{1}{2}(k_x - k_t)$ ; d) 0.0293 M added sodium acetate; e) 50 volume per cent acetic anhydride-acetic acid; f) 0.0510 M added 2,6-lutidine; g) extrapolated rate constants.



TABLE XVI

SOLVOLYSIS OF t-AMYLETHYLMETHYLSULFONIUM PERCHLORATE

Run	Solvent	Temp.	Isomer	Conc. (M)	$\mu$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_x^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )
2-177	EtOH	50	d1	0.01130	0.015	283 ± 9		
2-187	EtOH	50	(-)	0.01151	0.015	286 ± 6	1780±120	750 ± 70
2-221	EtOH	50	(+)	0.01154	0.015	268 ± 8	1830±220	780 ± 110
3-33	HOAc <sup>d</sup>	50	d1	0.01501	0.042	180 ± 8		
3-127	HOAc <sup>d</sup>	50	(-)	0.01559	0.042		1710± 20	770 ± 20
3-37	50%AcOAc <sup>de</sup>	50	d1	0.01504	0.042	130 ± 8		
3-135	50%AcOAc <sup>de</sup>	50	(-)	0.01501	0.042		1780± 30	820 ± 20
3-119	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	50	d1	0.01194	0.015	289 ± 5		
3-171	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	50	(-)	0.01176	0.015		2070±120	890 ± 60
2-179	EtOH	25	d1	0.01130	0.015	6.12±0.13		
2-189	EtOH	25	(-)	0.01151	0.015		63.1±1.2	28.5±0.6
3-35	HOAc <sup>d</sup>	25	d1	0.01501	0.042	4.36±0.17		
3-131	HOAc <sup>d</sup>	25	(-)	0.01559	0.042		51.0±0.7	22.8±0.5
3-39	50%AcOAc <sup>de</sup>	25	d1	0.01504	0.042	3.05±0.10		
3-137	50%AcOAc <sup>de</sup>	25	(-)	0.01501	0.042		52.5±0.9	24.7±0.5
3-121	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	25	d1	0.01194	0.015	6.25±0.22		
3-173	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	25	(-)	0.01176	0.015		57.9±1.2	25.8±0.7

a ) Titrimetric rate constant; b) polarimetric rate constant, runs in ethanol were done by Method I, all others by Method II; c)  $k_1 = \frac{1}{2}(k_x - k_t)$ ; d) 0.0293 M added sodium acetate; e) 50 volume per cent acetic anhydride-acetic acid; f) 0.0510 M added 2,6-lutidine.



TABLE XVII

SOLVOLYSIS OF 1-PHENYL-2-METHYL-2-PROPYLETHYLMETHYLSULFONIUM

PERCHLORATE

Run	Solvent	Temp.	Isomer	Conc. (M)	$\mu$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_x^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )
3-59	EtOH	50	d1	0.01189	0.015	47.8 ± 0.7		
3-203	EtOH	50	(-)	0.01169	0.015	47.1 ± 0.3	2220 ± 60	1080 ± 30
3-63	HOAc <sup>d</sup>	50	d1	0.01504	0.042	34.7 ± 0.7		
3-210	HOAc <sup>d</sup>	50	(-)	0.01527	0.042		2090 ± 40	1030 ± 20
3-67	50%AcOAc <sup>de</sup>	50	d1	0.01498	0.042	24.8 ± 0.3		
3-192	50%AcOAc <sup>de</sup>	50	(-)	0.01501	0.042		2110 ± 70	1040 ± 30
3-111	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	50	d1	0.01186	0.015	48.9 ± 1.6		
3-216	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	50	(-)	0.01161	0.015		2120 ± 40	1030 ± 20
3-61	EtOH	25	d1	0.01189	0.015	0.851 ± 0.014		
3-207	EtOH	25	(-)	0.01169	0.015		68.2 ± 1.6	33.7 ± 0.8
3-65	HOAc <sup>d</sup>	25	d1	0.01504	0.042	0.615 ± 0.024		
3-212	HOAc <sup>d</sup>	25	(-)	0.01527	0.042		59.5 ± 1.0	29.5 ± 0.5
3-69	50%AcOAc <sup>de</sup>	25	d1	0.01498	0.042	0.391 ± 0.017		
3-197	50%AcOAc <sup>de</sup>	25	(-)	0.01501	0.042		65.7 ± 0.7	32.7 ± 0.4
3-113	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	25	d1	0.01186	0.015	0.827 ± 0.009		
3-218	(CH <sub>3</sub> ) <sub>2</sub> CO <sup>f</sup>	25	(-)	0.01161	0.015		62.3 ± 1.1	30.7 ± 0.6

a) Titrimetric rate constant; b) polarimetric rate constant, runs in ethanol were done by Method I, all others by Method II;  
c)  $k_1 = \frac{1}{2}(K_x - K_t)$ ; d) 0.0293 M added sodium acetate; e) 50 volume per cent acetic anhydride-acetic acid; f) 0.0510 M added 2,6-lutidine.







rate of solvolysis of II (Table XV). The relative titrimetric rate constants at 50° are for ethanol : acetic acid : 50 volume per cent acetic anhydride-acetic acid : acetone are 1 : 0.69 : 0.49 : 0.91. The effect of solvent on the rate of racemization was less pronounced. The polarimetric rate constants are almost within experimental error of each other (Table XV).

t-Amylethylmethylsulfonium Perchlorate, III, and 1-Phenyl-2-methyl-2-propylethylmethylsulfonium Perchlorate, IV.

The titrimetric rate and polarimetric rate in ethanol at 50° has a half-life of 40 minutes and 6.5 minutes respectively for compound III and 4 hours and 5.2 minutes respectively for compound IV. Experiments were carried out to show that the loss of optical activity was due to racemization of the substrates (Run 2-208 and 3-189 for III and IV respectively). The melting points, n.m.r. and infrared spectra of the materials recovered indicated that they were the corresponding racemates. Again, loss of optical activity arises only by racemization and solvolysis.

As in the systems previously described, solvent has little effect on the rates of solvolysis of III of IV (Tables XVI and XVII). The relative titrimetric rate constants of III at 50° for ethanol : acetic acid : 50 volume per cent acetic anhydride-acetic acid and acetone are 1 : 0.64 :

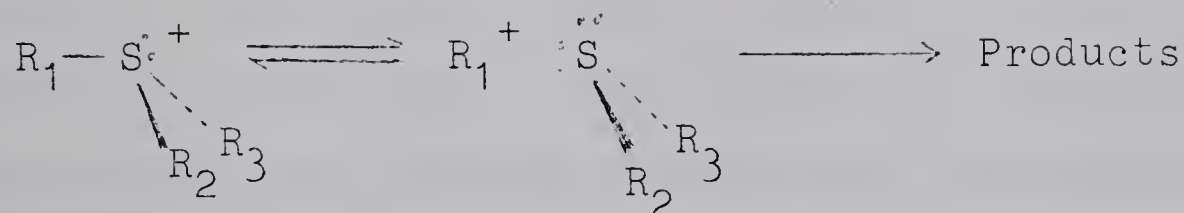


0.46 : 1.0. The relative titrimetric rate constants of IV for ethanol : acetic acid : 50 volume per cent acetic anhydride-acetic acid are 1 : 0.73 : 0.52 : 1.0.

The effect of solvent variation on the rates of racemization of III and IV was even less pronounced. The polarimetric rate constants are respectively almost within experimental error of each other (Tables XVI and XVII).

## DISCUSSION

We have seen in Chapter I that two mechanisms can account for the racemization of *t*-butylethylmethylsulfonium salts. (i) A heterolytic carbon-sulfur bond cleavage to form an ion-molecule pair which can either return to sulfonium salt or react with the solvent to yield substitution and/or elimination products.



(ii) A pyramidal inversion about the sulfur atom analogous to the inversion of the ammonia molecule.





A distinction between the two mechanisms can be made on the basis of substituent effects upon the reaction. In the first mechanism, both racemization and solvolysis occur through the same intermediate; therefore, substituents on the t-butyl group will affect both rates to a similar extent. Should mechanism (i) prevail then, to a first approximation, substitution of one of the hydrogens on the t-butyl group by an electron-withdrawing group will decrease the rate of carbon-sulfur bond heterolysis and hence reduce the rates of racemization and solvolysis by similar amounts. An electron-donating group will accelerate both rates by the opposite electronic effect. A second order effect will be steric in nature. Replacement of a hydrogen on one of the methyls of the t-butyl group by any other substituent may increase non-bonded interactions in the ground state. To the extent that these extra non-bonded interactions are relieved at the transition state, there will be a steric acceleration of the rate. This effect will occur whether the substituent is electron-withdrawing or electron-donating. Thus relief of strain may accelerate the rate of bond heterolysis to a small extent (66). Should mechanism (ii) prevail, then any substituent on the t-butyl group should either accelerate the rate of racemization by steric effects or have no effect whatsoever. The rate of solvolysis will still be governed by the factors that

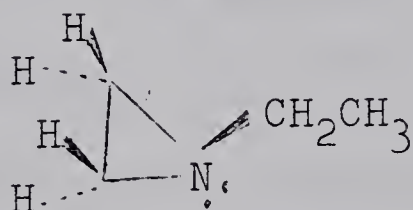




influence the rate of carbon-sulfur bond heterolysis as described above.

Kincaid and Henriques (33) have suggested that an increase in the size of the R groups attached to the central atom will decrease the height of the pyramid and thereby lower the activation energy required for inversion of the pyramid. Very recently, Miller et al. (65) have examined the limiting conditions of the Costain-Sutherland model (36) by varying the parameters involved and showed that the critical factors governing the inversion energy are the bending frequency,  $\nu_2$ , and the bond angle,  $\alpha$ .

The only available experimental data on the factors which affect the rate of inversion is that for the substituent effects on the rate of inversion of nitrogen in the aziridine series.



1-Ethylaziridine

Some of the results from the literature are reproduced in Table XVIII. Roberts and co-workers (67) have suggested that the large increase in the inversion rate of t-butyl-





TABLE XVIII  
NITROGEN INVERSION IN THE AZIRIDINE SERIES

Substituent	$T_c^a$	Reference
1-ethyl	108	67
1-ethyl	145 <sup>b</sup>	67
1- <u>t</u> -butyl	<-77	67
1-methyl-2,2-dimethyl	97	68
1-phenylethyl	96	67
2,2,3,3-tetramethyl	52	69
1-methyl- <u>trans</u> -2,3-dibenzoyl	-15	70
1-hydroxyethyl	83 <sup>c</sup>	71

a) Coalescence temperature ( $\pm 5^\circ$ ), ie. temperature at which  $k_{\text{inversion}} \approx 60 \text{ sec.}^{-1}$ . b) measured in  $D_2O$ . c) frequency, 20.509 mc.,  $k_{\text{inversion}} = 21.4 \text{ sec.}^{-1}$ .

aziridine was due to steric repulsions between the t-butyl group and the ring hydrogens. However this interpretation has been recently questioned by Anet and Osyani (72). They postulate that the single signal observed for the ring protons of t-butylaziridine at low temperature may be due to a small chemical shift,  $\nu_{ab}$ . So that as a result of



coupling a single line will be observed no matter what the value of  $k_{\text{inversion}}$  may be. They point out the fact that 1-methyl-2,2-dimethylaziridine has a much higher coalescence temperature even though the non-bonded interactions are similar. However they state that the high rate of inversion for 1-methyl-trans-2,3-dibenzoylaziridine and the fact that the trans isomer is less stable than the cis (70) are hard to explain by other than steric effects. The rate of inversion can be influenced by solvent. Roberts and Bottini (67) have shown that, in  $D_2O$ , the rate of inversion of 1-ethylaziridine is less than that for the neat liquid. Electronic factors may also affect the inversion rate. Electronegative substituents are expected to decrease the rate of inversion because of their tendency to increase the s character of the unshared pair on nitrogen (74). For a more complete discussion on the factors that influence the rate of pyramidal inversion, the reader may refer to articles by Bent (73) and by Anet, Terpka and Cram (74).

A summary of the rates of solvolysis and racemization of 1-R-2-methyl-2-propylethylmethylsulfonium perchlorates, I, II, III and IV, in ethanol is presented in Table XIX. The relative rates of ethanolysis are I : II : III : IV as 1 : 0.06 : 6.3 : 1.1 at  $50^\circ$  and 1 : 0.05 : 7.2 : 1.0 at  $25^\circ$  (Tables XX, XXIII). The effect of solvent variation on the relative rates of solvolysis of I, II, III and IV are



TABLE XIX

SOLVOLYSIS OF 1-R-2-METHYL-2-PROPYLETHYLMETHYLSULFONIUM  
PERCHLORATES (0.012 M) IN ANHYDROUS ETHANOL.  $\mu$  0.015.

Compd.	R	Temp.	$10^6 k_t^a$ (sec. <sup>-1</sup> )	$10^6 k_x^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )	$k_x/k_t$
I	H-	50	45.1 ± 0.6	471 ± 15	213 ± 8	11 ± 1
II	CH <sub>3</sub> O-	50	2.74 ± 0.03	805 ± 48	401 ± 24	300 ± 30
III	CH <sub>3</sub> -	50	286 ± 6	1780 ± 120	750 ± 70	6 ± 1
IV	C <sub>6</sub> H <sub>5</sub> -	50	47.1 ± 1.3	2220 ± 60	1080 ± 30	46 ± 2
I	H-	25	0.0857 ± 0.015	15.2 ± 1.3	7.2 ± 0.16	17 ± 2
II	CH <sub>3</sub> O-	25	0.0436 ± 0.002	27.0 ± 1.1	13.5 ± 0.6	620 ± 30
III	CH <sub>3</sub> -	25	6.12 ± 0.13	63.1 ± 1.2	28.5 ± 0.6	10 ± 1
IV	C <sub>6</sub> H <sub>5</sub> -	25	0.851 ± 0.014	68.2 ± 1.6	33.7 ± 0.8	80 ± 4

a) Titrimetric rate constant; b) Polarimetric rate constant;  
c)  $k_1 = \frac{1}{2}(k_x - k_t)$ .





TABLE XX

RELATIVE RATES OF SOLVOLYSIS AND RACEMIZATION OF 1-R-2-METHYL-2-PROPYLETHYLMETHYL-SULFONIUM PERCHLORATE IN A VARIETY OF SOLVENTS AT 50.00°.

Compd. R	Relative Rates of Solvolysis				Relative Polarimetric Rates			
	EtOH	HOAc	50%AcOAc	(CH <sub>3</sub> ) <sub>2</sub> CO	EtOH	HOAc	50%AcOAc	(CH <sub>3</sub> ) <sub>2</sub> CO
I H-	(1)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
II CH <sub>3</sub> O-	0.06	0.05	0.05	0.05	1.7	2.1	1.9	1.8
III CH <sub>3</sub> -	6.0	5.0	4.9	5.3	3.8	4.1	4.1	4.3
IV C <sub>6</sub> H <sub>5</sub> -	1.1	1.0	0.9	0.9	4.7	5.1	4.8	4.4



TABLE XXI

SOLVOLYSIS OF TERTIARY ALKYL CHLORIDES AT 25.00°

RC1	Solvent	$10^4 k$ (sec. <sup>-1</sup> )	$\Delta H^\ddagger$	$\Delta S^\ddagger$	Reference
(CH <sub>3</sub> ) <sub>3</sub> CCl	H <sub>2</sub> O	312	22.55	10.10	(76)
CH <sub>3</sub> OCH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> CCl	H <sub>2</sub> O	0.971	25.43	8.38	(77)
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> CCl	H <sub>2</sub> O	947 <sup>a</sup>	20.61	5.48	(77)
(CH <sub>3</sub> ) <sub>3</sub> CCl	80%EtOH	0.0914	22.6 <sup>b</sup>	-6 <sup>b</sup>	(79)
CH <sub>3</sub> CH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> CCl	80%EtOH	0.150	22.3 <sup>b</sup>	-6 <sup>b</sup>	(80, 81)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (CH <sub>3</sub> ) <sub>2</sub> CCl	80%EtOH	0.0190 <sup>a</sup>	22.9	-8.1	(81, 82)

a) Extrapolated values; b) values calculated from the reported Arrhenius energy,  $E_a$ .



TABLE XXII

EFFECT OF STRUCTURE ON THE RATES OF HYDROLYSIS OF DIETHYL  
ACETALS AND KETALS,  $RR_2C(OEt)_2$ , IN 49.6 WEIGHT PER CENT  
DIOXANE (78)

$R_1$	$R_2$	Log $k/k_0$	$\Sigma G^*$
$CH_3-$	$CH_3-$	0.000	0.000
$CH_3-$	$HOCH_2-$	-1.812	0.555
$CH_3-$	$C_6H_5OCH_2-$	-3.333	0.850
$CH_3-$	$CH_3CH_2-$	-0.03	-0.100
$CH_3-$	$C_6H_5CH_2-$	-0.851	0.225
H-	$CH_3-$	-3.482	0.450
H-	$HOCH_2-$	-5.949	1.045
H-	$CH_3CH_2OCH_2-$	-5.940	1.01
H-	$CH_3CH_2-$	-3.449	0.390
H-	$C_6H_5CH_2-$	-4.936	0.715



very small (Table XX). As expected, the electron-withdrawing methoxy group decelerates the rate of carbon-sulfur bond heterolysis and hence decreases the rate of solvolysis. The electron-donating methyl group accelerates the rate of carbon-sulfur bond heterolysis and hence increases the rate of solvolysis. Phenyl substitution has little effect on the rate of solvolysis.

The rate retardation by the methoxy group is quite small in comparison to the rate retardation by methoxy substitution in other systems. For example, Robertson and co-workers (77) have shown that introducing a methoxy group on t-butyl chloride decreases the rate of hydrolysis by a factor of 320 (Table XXI). Similarly, introducing an ethoxy or a hydroxy group on diethyl acetal decreases the rate of hydrolysis by a factor of 290 as shown by Kreevoy and Taft (75, 78). Their results are reproduced in Table XXII. For hydrolysis of t-butyl chloride, the neutral initial state becomes fully charged in the transition state. For hydrolysis of acetals and ketals, the neutral compound must first be protonated before decomposition. Both protonation and heterolysis will have substituent effects. The observed effect will be the sum of the substituent effects in both steps of the reaction. The net result is the observation of the conversion of a neutral compound to an ion. Therefore both, the hydrolysis of t-butyl halides and the decomposition of acetals





and ketals exhibit similar substituent effects. On the other hand, the solvolysis of sulfonium salts involves a charged species producing an ion in which the charge is closer to the substituent. This should be similar to the heterolysis of the protonated acetal. Since methoxy substitution decreases the rate of solvolysis of t-butylethylmethylsulfonium perchlorate by a factor of 20, the substituent effects for the protonation of acetals are equal to that for the heterolysis of the protonated acetal.

The rate of solvolysis of 1-phenyl-2-methyl-2-propyl chloride in 80 per cent ethanol-water at 25° is slower than that of t-butyl chloride by a factor of 5 (Table XXI). Vanderwerf (81, 82) states that this is consistent with the generalization that the phenyl group is electron-withdrawing. In contrast, phenyl substitution on the rates of solvolysis of t-butylethylmethylsulfonium perchlorate in a variety of solvents is negligible (Table XXIII).

The relative rates of racemization in ethanol at 50° are I : II : III : IV as 1 : 1.7 : 3.8 : 4.1. The effect of solvent variation on the relative rates of racemization of I, II, III and IV are very small (Table XX). Substituents on the t-butyl group of t-butylethylmethylsulfonium perchlorate accelerate the rate of racemization whether the group is electron-withdrawing or electron-donating (Tables XIX, XX). This effect cannot be electronic in origin but must be due to steric factors.



Methoxy substitution decreases the rate of solvolysis of t-butylethylmethylsulfonium perchlorate by a factor of ca. 20 whereas it causes an increase in the rate of racemization by a factor of ca. 2. To a first approximation, the increased rate constant for the racemization of II compared to I suggests that racemization must be independent of solvolysis and therefore requires that mechanism (ii) to be the correct explanation for racemization. However, this view may be an oversimplification. t-Butylethylmethylsulfonium perchlorate may not be a good model for 1-methoxy-2-methyl-2-propylethylmethylsulfonium perchlorate since steric effects could be important. Thus there still remains the possibility that electronic effects decelerating the rate of carbon-sulfur bond heterolysis are counterbalanced by larger steric effects which accelerate carbon-sulfur bond heterolysis. As a result, a net increase could be observed for the racemization of II. To discount this possibility the solvolysis of t-amylethylmethylsulfonium perchlorate was studied. A methyl group is approximately twice as large as a methoxy group as judged by the free energy differences between axial and equatorial substituents on cyclohexyl systems (83), but their electronic effects are opposite in nature. Methyl substitution increases the rate of racemization of t-butylethylmethylsulfonium perchlorate by a factor of 4 and increases the



TABLE XXIII

ETHANOLYSIS OF TERTIARY ALKYL SULFONIUM PERCHLORATES AT  
25.00°

$R-S^+(CH_3)(CH_2CH_3)ClO_4^-$	$10^6 k_t^a$ (sec. <sup>-1</sup> )	Relative Rates	$\Delta H^\ddagger$	$\Delta S^\ddagger$
$-C(CH_3)_3$	0.857	(1)	29.9±0.3	14± 1
$-C(CH_3)_2CH_2OCH_3$	0.0436	0.05	31.3±0.8	12± 3
$-C(CH_3)_2CH_2CH_3$	6.12	7.2	28.8±0.4	14± 1
$-C(CH_3)_2CH_2C_6H_5$	0.851	1.0	30.3±0.2	15± 1

TABLE XXIV

RACEMIZATION OF TERTIARY ALKYL SULFONIUM PERCHLORATES IN  
ETHANOL AT 25.00°

$R-S^+(CH_3)(CH_2CH_3)ClO_4^-$	$10^6 k^b$ (sec. <sup>-1</sup> )	$10^6 k_1^c$ (sec. <sup>-1</sup> )	$\Delta H^\ddagger$	$\Delta S^\ddagger$
$-C(CH_3)_3$	15.2	7.0	25.0±0.6	2 ± 2
$-C(CH_3)_2CH_2OCH_3$	27.0	13.5	25.4±0.8	4 ± 3
$-C(CH_3)_2CH_2CH_3$	63.1	28.5	24.5±0.2	3 ± 1
$-C(CH_3)_2CH_2C_6H_5$	68.2	33.7	26.0±0.4	8 ± 1

a) Titrimetric rate constants; b) polarimetric rate constants; c)  $k_1 = \frac{1}{2}(k_x - k_t)$ .







rate of solvolysis by a factor of 6. If we assume that all the rate acceleration of t-amylethylmethylsulfonium perchlorate is steric in nature, then methoxy substitution should give a rate acceleration of a factor of 2 to 3 by steric effects. This is small and of the order of observed kinetic effects on racemization. Therefore there cannot be large steric effects and large inductive effects counterbalancing each other. Consequently the inductive effects on the rate of racemization must be small.

The solvolysis and racemization of 1-phenyl-2-methyl-2-propylethylmethylsulfonium perchlorate was also studied. Phenyl substitution has no effect on the rate of solvolysis (Tables XIX, XX, XXIV). Clearly, the increase in the rate of racemization must be due to greater non-bonded interactions in the ground state relative to the planar or near-planar transition state.

The activation parameters for solvolysis and racemization of compounds I, II, III and IV in ethanol at 25° are listed in Tables XXIII and XXIV. We have seen that electronic effects and steric effects of substituents on the rate of solvolysis of t-butylethylmethylsulfonium perchlorate were small. Correspondingly, the enthalpies of activation are almost within experimental error of each other (Table XXIII). However the differences are consistent with theory in that methoxy substitution increases and methyl substitution decreases the enthalpy of acti-



vation but substituent effects are not as pronounced as in the corresponding chlorides (Table XXI). The entropies of activation for solvolysis are within experimental error of each other. The activation parameters for racemization, ie. inversion, of sulfonium salts are smaller than for solvolysis, ie. carbon-sulfur bond heterolysis (Table XXIV).

The results of substituent effects on the relative rates of racemization and solvolysis of tertiary sulfonium salts unequivocally indicate that the major portion of racemization of t-butylethylmethylsulfonium perchlorate involves inversion of the molecule about the central sulfur atom, and must be independent of carbon-sulfur bond heterolysis.

This work, a portion of which has been published (84, 85), represents the first evidence for the inversion of sulfur in sulfonium ions.

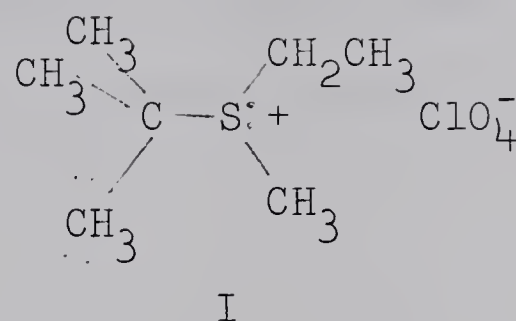
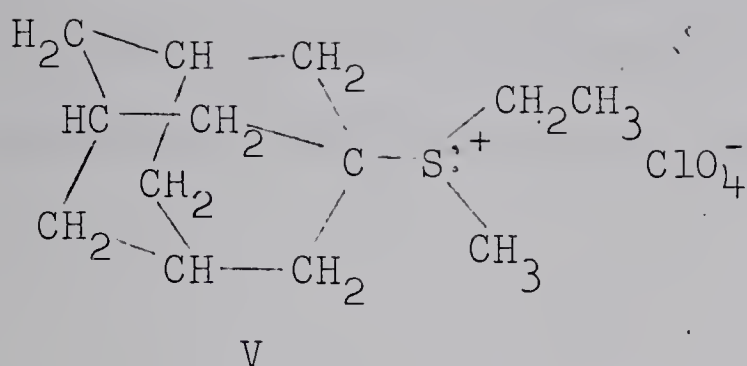
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Note added in proof

Mislow and Scartazzini (86) have tested and fully confirmed our conclusions. These authors investigated the racemization of 1-adamantylethylmethylsulfonium perchlorate. The steric effects of the 1-adamantyl and t-butyl groups are, to a first approximation, quite similar, whereas the stabilities of the corresponding carbonium ions were shown





by Schleyer and Nicholas (87) to differ by several orders of magnitude. As expected, V does not solvolyze under the conditions of racemization. In acetic acid at  $50^{\circ}$ , the rates of racemization of 1-adamantylethylmethylsulfonium perchlorate and *t*-butylethylmethylsulfonium perchlorate are  $8.59 \times 10^4 \text{ sec.}^{-1}$  and  $4.13 \times 10^4 \text{ sec.}^{-1}$  respectively. No isotopic exchange was observed upon racemization of 1-adamantylethyl- $d_5$ -methylsulfonium perchlorate in acetic acid in the presence of a 4.7 molar excess of ethyl methyl sulfide.

Since the polarimetric rate constants are comparable in magnitude even though the stabilities of the corresponding carbonium ions are different, racemization of I and V cannot involve carbon-sulfur bond heterolysis, but rather proceeds by inversion of the central sulfur atom.

The similar activation parameters obtained are consistent with this interpretation. The enthalpy and entropy of activation for the racemization of 1-adamantylethylmethylsulfonium perchlorate in acetic acid are 26 kcal.





per mole and 8 e. u. respectively (86),  $25.5 \pm 0.8$  kcal.

per mole and  $5 \pm 3$  e. u. respectively for the racemization  
of t-butylethylmethylsulfonium perchlorate in acetic acid.

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## EXPERIMENTAL

### REAGENTS AND MATERIALS

#### $\alpha$ -Bromoisobutyraldehyde

$\alpha$ -Bromoisobutyraldehyde was prepared from freshly distilled isobutyraldehyde by the procedure of Stevens and Gillis (64). Yield 260 g. (61 per cent), b.p. 110° at 700 mm.,  $n_D^{25}$  1.4514 (reported: (64) b.p. 111-112°,  $n_D^{25}$  1.4500; (88) b.p. 113-114°,  $n_D^{25}$  1.4518). N.m.r. (CDCl<sub>3</sub>):  $\tau$  8.19 (s, 6 H), 0.85 (s, 1 H). Infrared: 2815, 2710, 1720, 918 and 645 cm.<sup>-1</sup>. Ultraviolet (ethanol):  $\lambda_{\max}$  305 m $\mu$  (log  $\epsilon$  0.76).

#### Trimer of $\alpha$ -Bromoisobutyraldehyde

$\alpha$ -Bromoisobutyraldehyde, when allowed to stand at room temperature trimerizes. The reaction is catalyzed by traces of acid. The white crystalline needles were recrystallized from hot ethanol. M.p. 128-129° (reported (64): m.p. 129-130°). N.m.r. (CDCl<sub>3</sub>):  $\tau$  8.54 (s, 18 H), 5.09 (s, 3 H). Infrared: 2880 and 1115 cm.<sup>-1</sup>.

Anal. Calcd. for C<sub>12</sub>H<sub>21</sub>Br<sub>3</sub>O: C, 31.81; H, 4.67.

Found: C, 31.56, 31.96; H, 4.67, 4.88.

#### Reaction of $\alpha$ -Bromoisobutyraldehyde with 2,4-Dinitrophenylhydrazine

A solution of 1.5 g. (0.01 mole) of  $\alpha$ -bromoisobutyral-



dehyde was added to a freshly prepared solution of 2,4-dinitrophenylhydrazine hydrogen sulfate as described by Vogel (89). The yellowish-orange 2,4-dinitrophenylhydrazone was recrystallized from hot ethanol. Yield of  $\alpha$ -ethoxyisobutyraldehyde-2,4-dinitrophenylhydrazone was 2.4 g., (80 per cent). M.p.  $116^{\circ}$  (reported (64): m.p.  $116^{\circ}$ ). N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  8.79 (t,  $J=7.5$  cps., 3 H), 8.53 (s, 6 H), 6.54 (q,  $J=7.5$  cps., 2 H), 2.7-1.5 (m, 3 H), 0.84 (d,  $J=2.5$  cps., 1 H), -1.11 (s, 1 H). Stevens and Gillis (64) had proposed that the bromine is replaced by an ethoxy group during the reaction or its workup; the n.m.r. spectrum is consistent with their interpretation. Infrared: 3310, 3110, 1880, 1624, 1595, 1518, 1504, 1342, 1310, 1115, 1078, 928, 865 and 843  $\text{cm}^{-1}$ . Ultraviolet (ethanol):  $\lambda_{\text{max}}$  357  $\mu$  ( $\log \epsilon$  4.34); reported (64):  $\lambda_{\text{max}}$  357  $\mu$ .

Anal. Calcd. for  $\text{C}_{12}\text{H}_{16}\text{N}_4\text{O}_5$ : C, 48.65; H, 5.44; N, 18.91.

Found: C, 48.67, 49.00; H, 5.87, 5.77; N, 19.34, 19.22.

#### $\alpha$ -Ethylmercaptoisobutyraldehyde

Freshly cut sodium (25 g., 1.1 moles) was slowly added to a mixture of 250 ml. of reagent grade methanol and 150 ml. of anhydrous ethyl ether in a one-liter three-neck flask equipped with a stirrer, a dropping funnel and a condenser with drying tube. After the reaction had



subsided, ethyl mercaptan (67 g., 1.1 moles) was added dropwise followed by a solution of 140 g., (0.9 mole) of  $\alpha$ -bromoisobutyraldehyde in 150 ml. of ethyl ether. The mixture was refluxed for 30 minutes. Water (200 ml.) was added to dissolve the sodium bromide formed and the layers were separated in a one-liter separatory funnel. The ethereal layer was washed three times with 100 ml. portions of water, dried over anhydrous sodium sulfate and fractionally distilled through a 40 cm. Vigreux column. Yield 90 g. (73 per cent), b.p.  $154-155^{\circ}$  at 700 mm.,  $n_D^{25}$  1.4629. N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  8.87 (t,  $J=7.5$  cps., 3 H), 8.65 (s, 6 H), 7.67 (q,  $J=7.5$  cps., 2 H), 0.83 (s, 1 H). Infrared: 2820, 2720, 1710 and  $920\text{ cm}^{-1}$ . Ultraviolet (ethanol):  $\lambda_{\text{max}}$  211 m $\mu$  ( $\log \epsilon$  3.22).

Anal. Calcd. for  $\text{C}_6\text{H}_{12}\text{OS}$ : C, 54.50; H, 9.15.

Found: C, 54.20, 54.88; H, 9.25, 9.33.

Reaction of  $\alpha$ -Ethylmercaptoisobutyraldehyde with 2,4-Dinitrophenylhydrazine

The reaction of  $\alpha$ -mercaptoisobutyraldehyde with 2,4-dinitrophenylhydrazine in sulfuric acid was conducted as described above for  $\alpha$ -bromoisobutyraldehyde. The bright orange crystals were recrystallized from hot ethanol. Yield 2.4 g. (80 per cent), m.p.  $135.4-136.2^{\circ}$ . N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  8.80 (t,  $J=7.5$  cps., 3 H), 8.46 (s, 6 H), 7.52 (q,  $J=7.5$  cps., 2 H), 2.7-1.5 (m, 3 H), 0.85 (d,  $J=2.5$  cps., 1 H), -1.09 (s, 1 H). Infrared: 3310, 3160, 2880, 1624, 1596, 1518, 1505, 1342, 1330, 1310, 865, 843 and  $830\text{ cm}^{-1}$ .







Ultraviolet (ethanol):  $\lambda_{\max}$  365 m $\mu$  (log  $\epsilon$  4.36).

Anal. Calcd. for  $C_{12}H_{16}N_4O_4S$ : C, 46.14; H, 5.16; N, 17.94.

Found: C, 46.20, 46.32; H, 5.45, 5.55; N, 17.54, 17.71.

1-Hydroxy-2-methyl-2-propyl Ethyl Sulfide

A 6.0 g. (0.16 mole) quantity of lithium aluminum hydride and 500 ml. of anhydrous ethyl ether were placed in a one-liter three-neck flask equipped with a stirrer, a dropping funnel and a condenser with drying tube.  $\alpha$ -Ethylmercaptoisobutyraldehyde (72 g., 0.55 mole) was added at such a rate so that the ether refluxed gently. After the addition was complete, the mixture was refluxed for two hours. The excess hydride was decomposed by the careful addition of 12.0 ml. of water followed by 10.8 ml. of 10 per cent sodium hydroxide. The mixture was stirred for one hour, filtered and the solid residue was washed three times with 100 ml. portions of ethyl ether. The combined ether washings and filtrate were washed three times with water, dried over anhydrous sodium sulfate and fractionally distilled through a 40 cm. Vigreux column. Yield 54 g. (74 per cent), b.p. 179-180° at 700 mm.,  $n_D^{25}$  1.4553. N.m.r. ( $CDCl_3$ ):  $\tau$  8.77 (t,  $J=7.5$  cps., 3 H), 8.74 (s, 6 H), 7.51 (q,  $J=7.5$  cps., 2 H), 7.44 (s; 1 H), 6.62 (s, 2 H). Infrared: 3420, 1260 and 1050  $cm^{-1}$ .

Anal. Calcd. for  $C_6H_{16}OS$ : C, 53.68; H, 10.51.

Found: C, 53.87, 53.93, 54.22; H, 10.15, 10.64, 10.46.



Reaction of 1-Hydroxy-2-methyl-2-propyl Ethyl Sulfide with 3,4,5-Triiodobenzoyl Chloride

One gram (0.002 mole) of 3,4,5-triiodobenzoyl chloride (91) was added to an excess of 1-hydroxy-2-methyl-2-propyl ethylsulfide dissolved in anhydrous pyridine as described by Vogel (91). The resulting white precipitate was recrystallized from hot ethanol. Yield 0.8 g. (67 per cent), m.p. 130.2-131°. N.m.r. (dimethylsulfoxide- $d_6$ ):  $\tau$  8.87 (t,  $J=7.5$  cps., 3 H), 8.67 (s, 6 H), 7.5 (q, 2 H, some overlap by solvent impurities), 6.72 (s, 2 H), 1.67 (s, 2 H). Infrared: 3090, 3060, 1725, 1600, 1565, 1519, 1258, 1060, 1052, 891 and 870  $\text{cm}^{-1}$ . Ultraviolet: (ethanol)  $\lambda_{\text{max}}$  237  $\text{m}\mu$  ( $\log \epsilon$  4.44).

Anal. Calcd. for  $\text{C}_{13}\text{H}_{15}\text{I}_3\text{O}_2\text{S}$ : C, 25.35; H, 2.45.

Found: C, 25.56, 25.50, 25.41; H, 2.38, 2.44, 2.53.

1-Hydroxy-2-methyl-2-propylethylmethylsulfonium Iodide

A solution of 1-hydroxy-2-methyl-2-propyl ethyl sulfide (10.0 g., 0.075 mole) and iodomethane (10.4 g., 0.073 mole) in 30 ml. of nitromethane was allowed to stand in the dark at room temperature for 12 hours. A 60 ml. quantity of acetone was added and the mixture was placed in the freezer for several days. The solid product was filtered and recrystallized from a 4 : 1 acetone-ethyl ether. Yield 8.8 g. (61 per cent), m.p. 102° (dec.). N.m.r. ( $\text{D}_2\text{O}$ ):  $\tau$  8.44 (t,  $J=7.5$  cps., 3 H), 8.38 (s, 3 H), 7.08 (s, 3 H), 6.65 (q,  $J=7.5$  cps., 2 H), 6.07 (s, 2 H),



5.34 (s, 1 H). Infrared: 3310, 1262 and 1062  $\text{cm}^{-1}$

Anal. Calcd. for  $\text{C}_7\text{H}_{17}\text{IOS}$ : C, 30.44; H, 6.21.

Found: C, 30.26, 30.11; H, 6.34, 6.00.

1-Methoxy-2-methyl-2-propyl Ethyl Sulfide

Sodium hydroxide (11 g., 0.46 mole) was carefully added to 60 g. (0.45 mole) of 1-hydroxy-2-methyl-2-propyl ethyl sulfide dissolved in 300 ml. of anhydrous ethyl ether in a one-liter three-neck flask equipped with a stirrer, a dropping funnel and a condenser with drying tube. The mixture was stirred and refluxed for one hour. A 65 g. (0.46 mole) quantity of iodomethane was added and the mixture was allowed to reflux with stirring overnight. The mixture was washed three times with 200 ml. portions of water, dried over anhydrous sodium sulfate and fractionally distilled through a 40 cm. Vigreux column. Yield 57 g. (87 per cent), b.p. 87-88° at 65 mm.,  $n_D^{25}$  1.4535. N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  8.79 (t,  $J=7.5$  cps., 3 H), 8.72 (s, 6 H), 7.43 (q,  $J=7.5$  cps., 2 H), 6.71 (s, 2 H), 6.64 (s, 3 H). Infrared: 2815 and 1115  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_7\text{H}_{16}\text{OS}$ : C, 56.70; H, 10.88.

Found: C, 56.54, 56.91; H, 10.96, 11.00.

1-Methoxy-2-methyl-2-propylethylmethylsulfonium Iodide

A solution of 1-methoxy-2-methyl-2-propyl ethyl sulfide (46.0 g., 0.31 mole) and iodomethane (46.0 g., 0.32 mole) in 100 ml. of nitromethane was allowed to stand in the dark at room temperature for 5 hours. A 100 ml. quantity





of acetone was added and the mixture was placed in the freezer for several days. The solid product was filtered and recrystallized from a 1 : 1 acetone-ethyl ether solution. Yield 41.0 g. (44 per cent), m.p.  $77^{\circ}$  (dec.). N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  8.42 (t,  $J=7.5$  cps., 3 H); 8.28 (s, 6 H), 6.86 (s, 3 H), 6.52 (s, 2 H), 6.33 (q,  $J=7.5$  cps., 2 H). Infrared: 2818 and 1115  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_8\text{H}_{19}\text{IOS}$ : C, 33.11; H, 6.60.

Found: C, 33.25, 32.80; H, 6.46, 6.34.

(-)-1-Methoxy-2-methyl-2-propylethylmethylsulfonium 2R,3R-Dibenzoylhydrogentartrate

1-Methoxy-2-methyl-2-propylethylmethylsulfonium iodide (23.0 g., 0.08 mole) was converted to the corresponding dibenzoylhydrogentartrate by the procedure described in Chapter I for the preparation of t-butylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartrate. The racemic salt was recrystallized from a 500 ml. quantity of 3 : 2 methanol-ethyl ether to effect resolution. Yield 18.0 g. (43 per cent), m.p.  $122.4^{\circ}$  (dec.),  $[\alpha]_D^{25} -100$  ( $c$  0.645, methanol). Ultraviolet: (ethanol),  $\lambda_{\text{max}}$  230  $\text{m}\mu$  ( $\log \epsilon$  4.39). N.m.r. (dimethylsulfoxide- $d_6$ ):  $\tau$  8.65 (t,  $J=7.5$  cps., 3 H), 8.56 (s, 6 H), 7.17 (s, 3 H), 6.77 (q,  $J=7.5$  cps., 2 H), 6.67 (s, 3 H), 4.39 (s, 2 H), 2.5-2.1 (m, 10 H). Infrared: 3080, 3050, 3020, 2820, 1740, 1717, 1604, 1586, 1495, 1450, 1406, 1266, 1115, 726 and 707  $\text{cm}^{-1}$ .





Neut. Equiv. Calcd. for  $C_{26}H_{32}O_9S$ : 520.6. Found: 517.

Anal. Calcd. for  $C_{26}H_{32}O_9S$ : C, 59.98; H, 6.20.

Found: C, 59.99, 60.22; H, 6.19, 6.19.

dl-1-Methoxy-2-methyl-2-propylethylmethylsulfonium Perchlorate

dl-1-Methoxy-2-methyl-2-propylethylmethylsulfonium iodide (1.50 g., 0.0052 mole) was converted to the corresponding perchlorate using the same procedure as described in Chapter I for the preparation of dl-butylethylmethylsulfonium perchlorate. Yield 1.15 g. (85 per cent), m.p.  $103^{\circ}$  (dec.). N.m.r. ( $D_2O$ ):  $\tau$  8.54 (t,  $J=7.5$  cps., 3 H), 8.47 (s, 6 H), 7.19 (s, 3 H), 6.76 (q,  $J=7.5$  cps., 2 H), 6.54 (s, 3 H), 6.28 (s, 2 H). Infrared: 2810, 1115, 1090, 628 and 609  $cm^{-1}$ .

(-)-1-Methoxy-2-methyl-2-propylethylmethylsulfonium Perchlorate

(-)-1-Methoxy-2-methyl-2-propylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartrate (1.0 g., 0.002 mole), dissolved in 80 ml. of 80 per cent methanol-water, was converted to the corresponding hydroxide using a Dowex 1 x8 anion exchange resin as described for the preparation of t-butylethylmethylsulfonium bromide. The eluate was immediately neutralized with 5 per cent perchloric acid and the perchlorate salt was obtained and purified in the same manner as the racemate described above. Yield 0.4 g.



(80 per cent), m.p.  $102^{\circ}$  (dec.).  $[\alpha]_D^{25} -13.5$ ,  $[\alpha]_{436}^{25} -35.0$  (c 0.64 ethanol). The n.m.r. and infrared spectra were superimposable upon those of the corresponding racemic salt.

Anal. Calcd. for  $C_8H_{19}ClO S$ : C, 36.57; H, 7.29.

Found: C, 36.59, 36.37; H, 7.20, 7.13.

Racemization of (-)-1-Methoxy-2-methyl-2-propylethylmethylsulfonium Perchlorate

An aliquot of a solution of 0.284 g. of (-)-1-methoxy-2-methyl-2-propylethylmethylsulfonium perchlorate in 25 ml. of anhydrous ethanol and  $[\alpha]_D^{25} -0.105$  ( $l = 1$  dm.). The solution was transferred to ampoules which were sealed and placed in a  $25^{\circ}$  constant temperature bath for 120 hours (Run 3-166). This corresponds to 17 half-lives of racemization and 0.03 half-life of solvolysis. The optical rotation had decreased to 0.000. Ethyl ether was added until the solution became turbid and the mixture was placed in the freezer. The white precipitate, obtained by filtration, was dried in vacuo. Yield 0.19 g. (67 per cent). Melting point, n.m.r. and infrared spectra indicated that the material recovered was racemic 1-methoxy-2-methyl-2-propylethylmethylsulfonium perchlorate.

t-Amyl Ethyl Sulfide

t-Amyl ethyl sulfide was prepared from 70.4 g (0.8 mole) of t-amyl alcohol by the same procedure as described for the preparation of t-butyl ethyl sulfide. Yield 82 g.



(88 per cent), b.p.  $144-145^{\circ}$  at 698 mm.,  $n_D^{25}$  1.4498.

N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  9.05 (t,  $J=7.5$  cps., 3H), 8.77 (t,  $J=7.5$  cps., 3 H), 8.75 (s, 6 H), 8.44 (q,  $J=7.5$  cps., 2 H), 7.50 (q,  $J=7.5$  cps., 2 H). Ultraviolet (ethanol):  $\lambda_{\text{max}}$  214  $\mu$  (log 2.92).

Anal. Calcd. for  $\text{C}_7\text{H}_{16}\text{S}$ : C, 63.56; H, 12.19.

Found: C, 63.85, 63.61; H, 12.06, 12.08.

t-Amylethylmethylsulfonium Iodide

t-Amylethylmethylsulfonium iodide was obtained and purified in the same manner as described for the preparation of t-butylethylmethylsulfonium iodide. From 20.0 g.

(0.15 mole) of t-amyl ethyl sulfide, 20.0 g. (0.14 mole) of iodomethane in 30 ml. of nitromethane, 25 g. (65 per cent yield) of the iodide salt, m.p.  $101^{\circ}$  (dec.), was obtained. N.m.r. ( $\text{D}_2\text{O}$ ):  $\tau$  8.87 (t,  $J=7.5$  cps., 3 H), 8.44 (t,  $J=7.5$  cps., 3 H), 8.38 (s, 6 H), 8.02 (q,  $J=7.5$  cps., 2 H), 7.12 (s, 3 H), 6.70 (q, 7.5 cps., 2 H).

Anal. Calcd. for  $\text{C}_8\text{H}_{19}\text{IS}$ : C, 35.04; H, 6.98.

Found: C, 35.40, 35.15; H, 6.95, 6.87.

(-)-t-Amylethylmethylsulfonium 2R,3R-Dibenzoylhydrogen-tartrate

t-Amylethylmethylsulfonium iodide (11.0 g., 0.04 mole) was converted to the dibenzoylhydrogentartrate by the procedure described for the preparation of t-butylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartrate in Chapter







I. The racemic salt was recrystallized from a methanol-ethyl ether solution to effect resolution. Yield 5.0 g. (49 per cent), m.p.  $108.5^{\circ}$  (dec.),  $[\alpha]_D^{25} -104$  (c 2.61 methanol). Ultraviolet (ethanol):  $\lambda_{\max}$  229 m $\mu$  (log 4.94). N.m.r. (dimethylsulfoxide- $d_6$ ):  $\tau$  9.05 (t,  $J=7.5$  cps., 3 H), 8.64 (t,  $J=7.5$  cps., 3 H), 8.59 (s, 6 H), 8.20 (q,  $J=7.5$  cps., 2 H), 7.19 (s, 3 H), 6.70 (q,  $J=7.5$  cps., 2 H), 4.36 (s, 2 H), 2.7-2.3 (m, 6 H), 2.3-2.0 (m, 4 H). Infrared: 3085, 3060, 3030, 1727, 1710, 1672, 1602, 1587, 1492, 1450, 1401, 1258, 1115, 726 and 705  $\text{cm}^{-1}$ .

Neut. Equiv. Calcd. for  $\text{C}_{26}\text{H}_{32}\text{O}_8\text{S}$ : 504.6. Found: 500.

Anal. Calcd. for  $\text{C}_{26}\text{H}_{32}\text{O}_8\text{S}$ : C, 61.89; H, 6.39.

Found: C, 61.73, 61.84; H, 6.16, 6.15.

dl-t-Amylethylmethylsulfonium Perchlorate

dl-t-Amylethylmethylsulfonium perchlorate was prepared from 11.0 g. (0.04 mole) of the iodide by the same procedure described for the preparation of dl-t-butylethylmethylsulfonium perchlorate. Yield 6.5 g. (66 per cent), m.p.  $135^{\circ}$  (dec.). N.m.r. ( $\text{D}_2\text{O}$ ):  $\tau$  8.95 (t,  $J=7.5$  cps., 3 H), 8.52 (t,  $J=7.5$  cps., 3 H), 8.49 (s, 6 H), 8.11 (q,  $J=7.5$  cps., 2 H), 7.24 (s, 3 H), 6.71 (q,  $J=7.5$  cps., 2 H). Infrared: 1085, 627 and 606  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_8\text{H}_{19}\text{ClO}_4\text{S}$ : C, 38.94; H, 7.76.

Found: C, 38.60; H, 7.87.



(-)-t-Amylethylmethylsulfonium Perchlorate

(-)-t-Amylethylmethylsulfonium 2R,3R-dibenzoylhydrogentartrate (3.8 g., 0.0075 mole) was converted into the perchlorate salt in a manner similar to that described for the preparation of (-)-1-methoxy-2-methyl-2-propylethylmethylsulfonium perchlorate. Yield 1.7 g. (83 per cent)., m.p. 137° (dec.). N.m.r. and infrared spectra were superimposable upon those of the corresponding racemic salt.  $[\alpha]_D^{25} -25.1$ ,  $[\alpha]_{436}^{25} -50.1$  (c 0.431 methanol).

Anal. Calcd. for  $C_8H_{19}ClO_4S$ : C, 38.94; H, 7.76.

Found: C, 38.98, 38.67; H, 7.32, 7.67.

(+)-t-Amylethylmethylsulfonium Perchlorate

t-Amylethylmethylsulfonium perchlorate, enriched in the dextrorotary enantiomer, was prepared from the mother liquor obtained in the resolution of the dibenzoylhydrogentartrate salt. The mother liquors were concentrated and passed through a Dowex 1 x8 anion exchange resin, in its hydroxide form, in the same manner as described for the preparation of the salt enriched in its enantiomer. M.p. 137° (dec.),  $[\alpha]_D^{25} +15.7$  (c 0.415 methanol). N.m.r. and infrared spectra, as well as the rates of solvolysis and racemization in anhydrous ethanol were the same as those of the enantiomer thereby indicating that the dibenzoylhydrogentartrate was, at least partially, separated into its diastereomers.



Racemization of (-)-*t*-Amylethylmethylsulfonium Perchlorate

An aliquot of a solution of 0.0108 g. of (-)-*t*-Amylethylmethylsulfonium perchlorate in 25 ml. of methanol had  $n_D^{25}$  -0.108 ( $l = 1$  dm.). The solution was transferred to ampoules which were sealed and placed in a 25° constant temperature bath for 8 hours. This corresponds to 4 half-lives of racemization and 0.4 half-life of solvolysis. The optical rotation had decreased to 0.003. Ethyl ether was added until the solution became turbid and the mixture was placed in the freezer. The white precipitate, obtained by filtration was dried in vacuo. Yield 0.054 g. (50 per cent). Melting point, n.m.r. and infrared spectra indicated that the material recovered was racemic *t*-amylethylmethylsulfonium perchlorate.

1-Phenyl-2-methyl-2-propyl Ethyl Sulfide

A 50.0 g. (0.33 mole) quantity of 1-phenyl-2-methyl-2-propanol (K & K Laboratories "phenyl-tert-butanol") was converted to 61 g. (98 per cent yield) of 1-phenyl-2-methyl-2-propyl ethyl sulfide by the procedure described for the preparation of *t*-butyl ethyl sulfide. The compound had b.p. 134° at 16 mm.,  $n_D^{25}$  1.5321. N.m.r. (CDCl<sub>3</sub>):  $\tau$  8.82 (t,  $J=7.5$  cps., 3 H), 8.78 (s, 6 H), 7.55 (q,  $J=7.5$  cps., 2 H), 7.21 (s, 2 H), 2.86 (s, 5 H). Infrared: 3080, 3050, 3020, 1602, 1583, 1493, 735 and 694 cm.<sup>-1</sup>.





Anal. Calcd. for  $C_{12}H_{19}S$ : C, 74.16; H, 9.34.

Found: C, 74.5; H, 9.73.

1-Phenyl-2-methyl-2-propylethylmethylsulfonium Iodide

1-Phenyl-2-methyl-2-propyl ethyl sulfide (15.0 g., 0.077 mole) was added to 11.0 g. (0.077 mole) of iodo-methane in 20 ml. of nitromethane. 1-Phenyl-2-methyl-2-propylethylmethylsulfonium iodide was obtained and purified by the procedure described for the preparation of t-butylethylmethylsulfonium iodide. Yield 24.0 g. (92 per cent), m.p.  $114^{\circ}$  (dec.). N.m.r. ( $CDCl_3$ ):  $\tau$  8.47 (t,  $J=7.5$  cps., 3 H), 8.39 (s, 6 H), 6.93 (s, 3 H), 6.74 (s, 2 H), 6.48 (q,  $J=7.5$  cps., 2 H), 2.73 (s, 5 H). Infrared: 3080, 3050, 3020, 1602, 1582, 1490, 734 and 700  $cm.^{-1}$ .

Anal. Calcd. for  $C_{13}H_{21}IS$ : C, 46.43; H, 6.29.

Found: C, 46.64, 46.44; H, 6.56, 6.23.

(-)-1-Phenyl-2-methyl-2-propylethylmethylsulfonium 2R, 3R-Dibenzoylhydrogentartrate

1-Phenyl-2-methyl-2-propylethylmethylsulfonium iodide (16.0 g., 0.048 mole) was converted to the dibenzoylhydrogentartrate salt by the procedure described for the preparation of t-butylethylmethylsulfonium 2R, 3R-dibenzoylhydrogentartrate. The dibenzoylhydrogentartrate was recrystallized from a 400 ml. of 1 : 1 acetone-ethyl ether solution to effect resolution. Yield 3.6 g. (27 per cent), m.p.  $98^{\circ}$  (dec.),  $[\alpha]_D^{25} -83$  (c





0.560, methanol). N.m.r. (dimethylsulfoxide- $d_6$ ):  $\tau$  8.65 (t,  $J=7.5$  cps., 3 H), 8.60 (s, 6 H), 7.11 (s, 3 H), 6.89 (s, 2 H), 6.73 (q,  $J=7.5$  cps., 2 H), 4.37 (s, 2 H), 2.72 (s, 5 H), 2.7-2.4 (m, 6 H); 2.2-2.0 (m, 4 H).

Infrared: 3080, 3050, 3020, 1740, 1710, 1670, 1603, 1586, 1493, 1396, 1263, 1110, 726 and 704  $\text{cm}^{-1}$ .

Neut. Equiv. Calcd. for  $\text{C}_{31}\text{H}_{34}\text{O}_8\text{S}$ : 566.7. Found: 570.

Anal. Calcd. for  $\text{C}_{31}\text{H}_{34}\text{O}_8\text{S}$ : C, 65.70; H, 6.42.

Found: C, 65.35, 65.38; H, 6.42, 6.34.

dl-1-Phenyl-2-methyl-2-propylethylmethylsulfonium Perchlorate

dl-1-Phenyl-2-methyl-2-propylethylmethylsulfonium perchlorate was prepared from 17.0 g. (0.051 mole) of the iodide salt by the procedure described for the preparation of dl-t-butylethylmethylsulfonium perchlorate. However it was recrystallized from a 260 ml. quantity of methanol. Yield 9 g. (58 per cent), m.p.  $104^{\circ}$  (dec.). N.m.r.

(dimethylsulfoxide- $d_6$ ):  $\tau$  8.61 (t,  $J=7.5$  cps., 3 H), 8.57 (s, 6 H), 7.10 (s, 3 H), 6.87 (s, 2 H), 6.72 (q,  $J=7.5$  cps., 2 H), 2.67 (s, 5 H). Infrared: 3075, 3050, 3020, 1604, 1580, 1493, 1085, 732, 700, 628 and 608  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{13}\text{H}_{21}\text{ClO}_4\text{S}$ : C, 50.56; H, 6.86.

Found: C, 50.27, 50.49; H, 6.75, 6.66.

(-)-1-Phenyl-2-methyl-2-propylethylmethylsulfonium Perchlorate

(-)-1-Phenyl-2-methyl-2-propylethylmethylsulfonium



2R,3R-dibenzoylhydrogentartrate (3.0 g., 0.0053 mole) was converted into (-)-1-phenyl-2-methyl-2-propylethyl-methylsulfonium perchlorate by the procedure described for the preparation of (-)-1-methoxy-2-methyl-2-propylethyl-methylsulfonium perchlorate. Yield 1.4 g. (86 per cent), m.p.  $106^{\circ}$  (dec.),  $[\alpha]_D^{25} -11.0$ ,  $[\alpha]_{436}^{25} -21.4$  (c 0.528, methanol). N.m.r. and infrared spectra were superimposable upon those of the racemate.

Anal. Calcd. for  $C_{13}H_{21}ClO_4S$ : C, 50.56; H, 6.86.

Found: C, 50.53, 50.90; H, 6.51, 6.84.

Racemization of (-)-1-Phenyl-2-methyl-2-propylethyl-methylsulfonium Perchlorate

An aliquot of a solution of 0.132 g. (-)-1-phenyl-2-methyl-2-propylethylmethylsulfonium perchlorate in 25 ml. of methanol had  $[\alpha]_D^{25} -0.113$  ( $d = 1$  dm.). The solution was transferred to ampoules which were sealed and placed in a  $25^{\circ}$  constant temperature bath for 48 hours (Run 3 -189). This corresponds to 17 half-lives of racemization and 0.2 half-life of solvolysis. The optical rotation had decreased to 0.000. Ethyl ether was added until the solution became turbid and the mixture was placed into the freezer. The white precipitate, obtained by filtration, was dried in vacuo. Yield 0.100 g. (88 per cent). Melting point, n.m.r. and infrared spectra indicated that the material recovered was racemic 1-phenyl-2-methyl-2-propylethylmethylsulfonium perchlorate.



## KINETIC ANALYSES

The procedure followed for the measurement of titrimetric and polarimetric rates for the solvolysis of 1-methoxy-2-methyl-2-propylethylmethylsulfonium perchlorate, II, t-amylethylmethylsulfonium perchlorate, III, and 1-phenyl-2-methyl--2-propylethylmethylsulfonium perchlorate, IV, was similar to that described for the solvolysis of t-butylethylmethylsulfonium perchlorate I.





### CHAPTER III

#### PRODUCT ANALYSES

In Chapter II, the excess of racemization over solvolysis was shown to be independent of the solvolysis reaction and its mechanism was elucidated. In this chapter, a further consideration will be made of the mechanism of solvolysis of sulfonium salts. In particular, the analysis of the products of solvolysis was undertaken and the information obtained from these studies will be discussed.

#### RESULTS

The solvolysis of tertiary sulfonium salts produces varying amounts of substitution and elimination products depending upon the solvent and reaction conditions. Each mole of sulfonium salt produced one mole of ethyl methyl sulfide and one mole of acid upon solvolysis. The amount of acid was determined by titration and the amount of the other products was determined by gas chromatography. For the solvolysis of t-butylethylmethylsulfonium and t-amylethylmethylsulfonium salts, the products were not isolated from the solvent but rather the reaction solution was injected directly into the Vapor Fractometer (Method II). For the solvolysis of 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts, the products were extracted from the solution before injecting a sample into the



Vapor Fractometer (Method I). Details of the analyses by Methods I and II are presented in the Experimental section.

The acid produced must be neutralized as it is formed in order to prevent acid-catalyzed addition of the solvent to the olefins produced. For this purpose an excess of 2,6-lutidine and an excess of sodium acetate were added to the ethanol and acetic acid solutions respectively.

An accurately known amount of internal standard was added to each solution in order to ascertain the per cent recovery. The area of each component peak relative to the peak area of the internal standard was calculated using a Honeywell Disc Chart Integrator.

A series of control solutions containing various ratios of each product relative to the internal standard were prepared and analyzed in exactly the same manner as the product analyses in order to calibrate the analytical method. Standardization curves were constructed by plotting the weight of each component per 25 ml. of solution calculated from the relative peak areas vs their known concentrations. Refer to the Experimental section for a detailed description of typical analyses.

#### t-Butylethylmethylsulfonium Salts

A summary of the ratios obtained from the solvolysis of t-butylethylmethylsulfonium salts in ethanol and acetic acid at 70° is presented in Tables XXV and XXVII respec-



tively. It is immediately obvious that the fraction of elimination is dependent upon the solvent and upon the anion present in the solution. The fraction of elimination from the sulfonium bromide (Run 4-10) is much larger than that from the sulfonium perchlorate (Run 4-8). Addition of chloride or acetate anions to the ethanolysis of the sulfonium perchlorate causes an increase in the fraction of elimination (Runs 4-12, 4-21 and 4-52). However the addition of lithium perchlorate has no effect on the product distribution (Run 4-70). Addition of a 20 molar excess of dimethyl sulfide has little effect on the product ratios from the ethanolysis of the sulfonium perchlorate (Run 4-54).

Analyses of aliquots removed during ethanolysis of t-butylethylmethylsulfonium perchlorate with added lithium chloride indicate, as shown in Table XXVI, that t-butyl chloride is formed during solvolysis. The amount of t-butyl chloride observed increases to a maximum of 11 mole per cent and then decreases as t-butyl chloride itself solvolyzes.

Changing the solvent from ethanol to acetic acid results in an increase in the fraction of elimination from the solvolysis of the sulfonium bromide (Table XXVII, Run 3-266). However a decrease in the fraction of elimination is observed for the solvolysis of the sulfonium perchlorate (Table XXVII, Run 3-264). The product composition for solvolysis in 50 volume per cent acetic anhydride-





TABLE XXV

PRODUCT ANALYSIS OF t-BUTYLETHYLSULFONIUM SALTS AND t-BUTYL CHLORIDE WITH 0.050 M

ADDED 2,6-LUTIDINE IN ETHANOL AT 70.00°

Run	Compound	Conc. M	Added	M	Time hrs.	Iso- butene	Products (mole per cent)	H <sup>+</sup> a	<u>t</u> BuCl
							<u>t</u> BuOEt	EtSMe	
4-8	<u>t</u> BuEtMeSClO <sub>4</sub>	0.01495			3.2	20 ±2	81 ±1	100 ±2	100 ±2
4-10	<u>t</u> BuEtMeSBr	0.01564			3.2	40 ±1	61 ±1	98 ±2	100 ±2
4-12	<u>t</u> BuEtMeSClO <sub>4</sub>	0.01602	LiCl	0.01738	3.2	33 ±1	62 ±1	98 ±1	98 ±1
4-21	<u>t</u> BuEtMeSClO <sub>4</sub>	0.01585	LiCl	0.1527	3.1	51	47	101	96
4-21	<u>t</u> BuEtMeSClO <sub>4</sub>	0.01585	LiCl	0.1527	3.1	53	49	100	97
4-70	<u>t</u> BuEtMeSClO <sub>4</sub>	0.01683	LiClO <sub>4</sub>	0.07660	3.2	21 ±1	78 ±2	101 ±1	99 ±1
4-52	<u>t</u> BuEtMeSClO <sub>4</sub>	0.01674	NaOAc	0.1021	5	59	37	97	
4-52	<u>t</u> BuEtMeSClO <sub>4</sub>	0.01674	NaOAc	0.1021	24	62	38	98	
4-54	<u>t</u> BuEtMeSClO <sub>4</sub>	0.02335	MeSMe	0.4335	5	24 ±2	76	100 ±1	101 ±1
4-64	<u>t</u> BuCl	0.02070			39	46 ±1	52 ±2		98 ±1
4-66	<u>t</u> BuCl	0.02070	LiCl	0.1335	39	54 ±2	49 ±1		98 ±1
4-68	<u>t</u> BuCl	0.02070	KOAc	0.1035	39	53 ±2	50 ±2		

a) Obtained by titration.





TABLE XXVI

PRODUCT ANALYSES OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE (0.01585 M) WITH ADDED LITHIUM CHLORIDE (0.1527 M) AND 2,6-LUTIDINE (0.05123 M) IN ANHYDROUS ETHANOL AT 70.00°. RUN 4-21.

Run	Time (min.)	Products (mole per cent)				
		Isobutene	<u>t</u> -BuCl	<u>t</u> -BuOEt	EtSMe	H <sup>+</sup> a
4-21.2	4	5	1	6	15	14
4-21.3	12	20	7	21	44	43
4-21.4	20	35	6	35	75	68
4-21.5	36	42	10	40	93	84
4-21.6	64	45	11	43	97	93
4-21.7	184	51	7	47	101	96
4-21.8	1380	53	1	49	100	97

a) Obtained by titration.



acetic acid is within experimental error of the product composition for solvolysis in 100 per cent acetic acid (Table XXVII, Runs 3-265, 3-267).

Analyses of aliquots removed during acetolysis of t-butylethylmethylsulfonium perchlorate with added lithium acetate and lithium chloride indicate that t-butyl chloride formed during the reaction increases to a maximum of 27 per cent and then decreases as the t-butyl chloride solvolyzes under the reaction conditions (Table XXVIII, Run 4-26).

#### t-Amylethylmethylsulfonium Perchlorate

The product distribution for the ethanolysis and acetolysis of t-amylethylmethylsulfonium salts at 50° is presented in Table XXIX. The effect of solvent and anion on the solvolysis of t-amyl sulfonium salts was similar to that observed for the corresponding t-butylsulfonium salts. For ethanolysis of the sulfonium perchlorate and iodide, the fractions of elimination were 0.22 and 0.66 respectively. Changing the solvent to acetic acid caused a small decrease in the fraction of elimination for the perchlorate. As expected, the more highly substituted olefin, 2-methylbutene, was produced in higher yield than 1-methyl-2-butene. The fractions of 1-methyl-2-butene (0.13) and 2-methyl-2-butene (0.53) for the ethanolysis of t-amylethylmethylsulfonium iodide were similar to those reported



TABLE XXVII

PRODUCT ANALYSES FOR t-BUTYLETHYLMETHYLSULFONIUM SALTS IN ACETIC ACID AT 70.00°

Run	Solvent	Anion Conc. M	Added base	M	LiCl	Time hrs.	Iso- butene	Products (mole per cent)			
								tBuCl	tBuOAc	EtSMe	H <sup>+</sup> a
3-264	HOAc	ClO <sub>4</sub> <sup>-</sup>	0.01400	NaOAc	0.0305	5.8	12 ±1	87 ±1	98±4	98±1	
3-265	AcOAc	ClO <sub>4</sub> <sup>-</sup>	0.01400	NaOAc	0.0305	5.8	13 ±1	84 ±1	99±2	97±1	
4-26.6 <sup>c</sup>	HOAc	ClO <sub>4</sub> <sup>-</sup>	0.01581	LiOAc	0.0637	0.7	34	25	92		
4-26.9 <sup>c</sup>	HOAc	ClO <sub>4</sub> <sup>-</sup>	0.01581	LiOAc	0.0637	7.2	47	11	100		
3-266	HOAc	Br <sup>-</sup>	0.01659	NaOAc	0.0305	5.8	68 ±3	35 ±4	102±1	100±1	
3-267	AcOAc	Br <sup>-</sup>	0.01659	NaOAc	0.0305	5.8	68 ±1	37 ±2	100±1	94±1 <sup>d</sup>	

a) Obtained by titration; b) 50 volume per cent acetic anhydride-acetic acid; c) refer to Table XXVIII; d) titration end-point is not sharp in this solvent.





TABLE XXVIII

PRODUCT ANALYSES OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE  
(0.01581 M) WITH ADDED LITHIUM ACETATE (0.06372 M) AND  
LITHIUM CHLORIDE (0.1602 M) IN ANHYDROUS ACETIC ACID AT  
70.00°. Run 4-26.

Run	Time (min.)	Products (mole per cent)			
		Isobutene	<u>t</u> -BuCl	<u>t</u> -BuOAc	EtSMe
4-26.1	4	4	6	-	18
4-26.2	8	8	10	7	29
4-26.3	13	22	13	12	49
4-26.4	20	25	20	15	61
4-26.5	28	27	20	19	73
4-26.6	40	34	25	31	92
4-26.7	56	36	27	32	97
4-26.8	250	45	13	42	102
4-26.9	430	47	11	42	100



by Ingold and co-workers (11) for ethanolysis of t-amyl-dimethylsulfonium iodide, 0.084 and 0.561 respectively.

1-Phenyl-2-methyl-2-propylethylmethylsulfonium Salts

Results of the product analyses for the solvolysis of 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts are presented in Table XXX. The fractions of elimination for ethanolysis of the perchlorate and iodide are 0.37 and 0.75 respectively. As expected, the more highly substituted and more highly conjugated olefin, 1-phenyl-2-methylpropene, is produced in greater yield than 3-phenyl-2-methylpropene. Addition of lithium chloride (Run 4-72) increases the fraction of elimination for ethanolysis of IV. The fractions of 1-phenyl-2-methylpropene and 3-phenyl-2-methylpropene were 0.21 and 0.51 respectively. Bunnett (94) and co-workers reported 0.245 and 0.343 respectively for the methanolysis of 1-phenyl-2-methyl-2-propyl chloride in the presence of 2,6-lutidine and 2,6-lutidinium chloride. Changing the solvent from ethanol to acetic acid causes a small decrease in the fraction of elimination for the sulfonium perchlorate but diverts the entire reaction of the sulfonium iodide through elimination



TABLE XXIX

PRODUCT ANALYSES OF t-AMYLETHYLMETHYLSULFONIUM SALTS AT 50.00°

Run	Solvent	Salt	M	$\begin{array}{c} \text{Et} \quad \text{H} \quad \text{Me} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Me} \quad \text{H} \quad \text{Me} \end{array}$	$\begin{array}{c} \text{Me} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array}$	Products (mole per cent)	EtSMe	H <sup>+</sup> a
4-14	EtOH <sup>be</sup>	ClO <sub>4</sub> <sup>-</sup>	0.01590	6 ± 1	16 ± 1	77 ± 1	98 ± 1	99 ± 1
4-60	EtOH <sup>be</sup>	I <sup>-</sup>	0.01322	13 ± 1	53 ± 1	28 ± 2	98 ± 1	
3-262	HOAc <sup>cf</sup>	ClO <sub>4</sub> <sup>-</sup>	0.01546	4 ± 1	16 ± 1	83 ± 1	98 ± 2	100 ± 1
3-263	AcOAc <sup>cdf</sup>	ClO <sub>4</sub> <sup>-</sup>	0.01546	5 ± 1	17 ± 1	80 ± 5	99 ± 1	99 ± 1

a) Obtained by titration; b) 0.050 M added 2,6-lutidine; c) 0.031 M added sodium acetate; d) 50 volume per cent acetic anhydride-acetic acid; e) standard: methylene chloride 0.02 M; f) standard: benzene 0.017 M.



TABLE XXX

PRODUCT ANALYSES OF 1-PHENYL-2-METHYL-2-PROPYLETHYLMETHYLSULFONIUM SALTS AT 70.00°

Run	Solvent	Salt	M	Base M	$\phi\text{CH}_2$	$\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{Me} \end{array}$	$\begin{array}{c} \text{H} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{H} \end{array}$	$\phi$	$\begin{array}{c} \text{Me} \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{Me} \end{array}$	Products (mole per cent)			
									$\phi\text{CH}_2$	$\begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OEt} \end{array}$	$\begin{array}{c} \text{Me} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OAc} \end{array}$	$\begin{array}{c} \text{EtSMe} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H}^{+a} \end{array}$	
4-40	EtOH	$\text{ClO}_4^-$	0.01555	0.05044 <sup>b</sup>	16 ± 1	21 ± 1	63 ± 1	99 ± 1	99 ± 1				
4-44	EtOH	$\text{I}^-$	0.01281	0.05044 <sup>b</sup>	22 ± 1	53 ± 1	24 ± 1	99 ± 2					
4-72	EtOH	$\text{ClO}_4^-$	0.01594 <sup>d</sup>	0.05053 <sup>bd</sup>	21 ± 1	51 ± 1	28 ± 1	99 ± 2					
4-42	HOAc	$\text{ClO}_4^-$	0.01614	0.03052 <sup>c</sup>	13 ± 1	15 ± 1	69 ± 2	100 ± 3	98 ± 1				
4-46	HOAc	$\text{I}^-$	0.01307	0.03052 <sup>c</sup>	28 ± 1	67 ± 1							

a) Obtained by titration; b) 2,6-lutidine; c) NaOAc; d) 0.1330 M added lithium chloride.





## DISCUSSION

Hughes and Ingold (2) reported that the solvolysis of t-butyl chloride, bromide, iodide and dimethylsulfonium iodide in 80 per cent aqueous ethanol produced the same amount of olefin even though the rate varied more than one thousand-fold. Winstein and Cocivera (23) have re-examined the solvolysis of these compounds in anhydrous ethanol and acetic acid. They found that in these solvents the fraction of elimination depended upon the nature of the leaving group. A comparison of their results, reproduced in Table XXXI, with the results of the present work (Tables XXV, XXVII) shows that replacing one of the

TABLE XXXI

MOLE PER CENT OLEFIN FROM SOLVOLYSIS IN SEVERAL SOLVENTS  
AT 75.0°. (23)

X <sup>a</sup>	H <sub>2</sub> O <sup>b</sup>	EtOH <sup>b</sup>	AcOH <sup>c</sup>
<u>t</u> -Butyl chloride	7.6 ± 1.0	44.2 ± 1.0	73 ± 2
<u>t</u> -Butyl bromide	6.6 ± 1.0	36.0 ± 1.0	69.5
<u>t</u> -Butyl iodide	6.0 ± 1.0	32.3 ± 1.0	
<u>t</u> -Butyl SMe <sub>2</sub> <sup>+</sup> ClO <sub>4</sub> <sup>-</sup>	6.5 ± 1.0	17.8 ± 1.4	11.7 ± 1.0
<u>t</u> -Butyl OH <sub>2</sub> <sup>+</sup>	4.7		
<u>t</u> -Amyl chloride	8.9 ± 0.4		85

a) ca. 0.04 M.; b) 0.07-0.14 M. 2,6-lutidine; c) 0.025-0.103 M. NaOAc.



methyl groups on t-butyldimethylsulfonium perchlorate by an ethyl group has very little effect on the product distribution. More pertinent is the fact that the product distribution from the solvolysis of t-butylethylmethylsulfonium salts is strongly influenced by the anion present in the solution.

The ethanolysis of t-butylethylmethylsulfonium bromide results in a product distribution that is radically different from the product distribution observed for the ethanolysis of t-butylethylmethylsulfonium perchlorate but similar to the product distribution observed by Cocivera and Winstein (23) for the ethanolysis of t-butyl bromide. Changing the solvent from ethanol to acetic acid causes a decrease in the fraction of elimination for the solvolysis of the sulfonium perchlorate. In contrast, changing the solvent from ethanol to acetic acid results in an increase in the fraction of elimination from the solvolysis of sulfonium bromide and t-butyl bromide. The results strongly suggest that the products of the solvolysis of t-butylethylmethylsulfonium bromide and t-butyl bromide arises from the same or similar intermediates.

The addition of lithium chloride to t-butylethylmethylsulfonium perchlorate in solvents ethanol and acetic acid also produced a marked change in the fraction of olefin produced. For ethanolysis in the presence of 0.153 M lithium chloride, the fraction of olefin produced



is 0.53. This is larger than the fraction of olefin produced from ethanolysis of t-butyl chloride (0.44, Table XXXI). It is similar to the fraction of olefin produced when t-butyl chloride is subjected to ethanolysis in the presence of 0.133 M lithium chloride (0.54, Table XXV). An increase in the fraction of olefin is also observed for ethanolysis of t-butylethylmethylsulfonium perchlorate and t-butyl chloride in the presence of acetate anion. However, the addition of perchlorate anion has no effect on the rate or product distribution for the ethanolysis of t-butylethylmethylsulfonium perchlorate (Tables V, XXV).

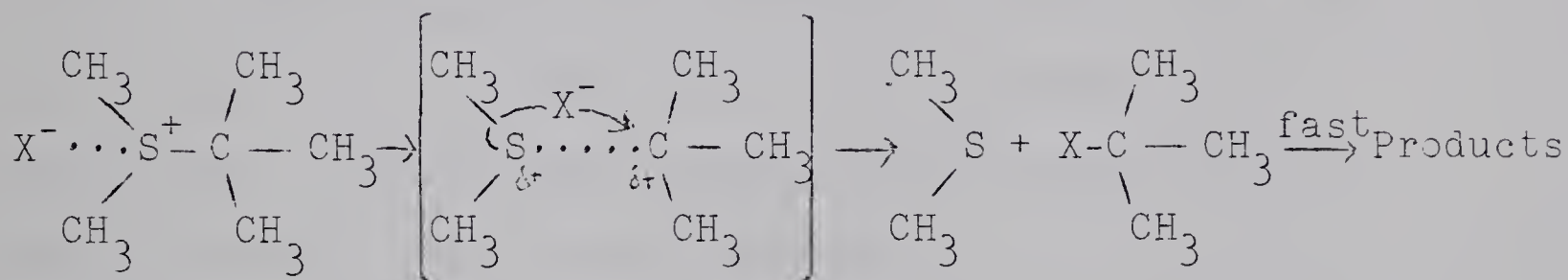
In view of the marked effect of the anion of the product distribution, the free t-butyl cation cannot be the intermediate which undergoes reaction with the solvent to give substitution and elimination products. The anion must be involved in the reaction. These observations point up the fact that the difference in the product ratios observed by Winstein (23) and Ingold (11) arose entirely from their choice of anions which were associated with the sulfonium salts.

One method of accounting for these observations would involve the assumption that the first step in the solvolysis of the sulfonium salt in the presence of halide anion is the formation of the corresponding alkyl halide.





The alkyl halide would then give the same product distribution as that found when it is solvolyzed directly. That is, the alkyl halide would be a common intermediate in the solvolysis of both, sulfonium halide salts and alkyl halides. Hyne and Abrell (18) proposed that in media of low dielectric the solvolysis of t-butyldimethylsulfonium salts proceeds through an ion-pair, composed of the sulfonium salt and its anion, by an  $S_N1$  mechanism involving intramolecular nucleophilic attack of the halide on the t-butyl carbon atom to displace the sulfide group and form t-butyl halide which, under the conditions of the reaction, reacts further to produce elimination and substitution products.



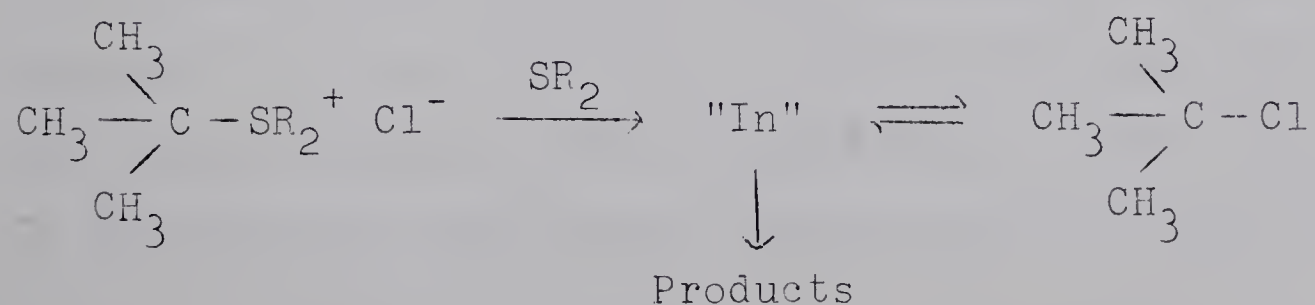
Gas chromatographic analyses of samples from the solvolysis of t-butylethylmethylsulfonium perchlorate with added lithium chloride in ethanol and acetic acid at 70° indicate, as shown in Tables XXVI and XXVIII, that t-butyl chloride is indeed formed during solvolysis. At 70°, the rates of solvolysis of t-butylethylmethylsulfonium perchlorate with no added salt are  $(7.28 \pm 0.50) \times 10^{-4} \text{ sec.}^{-1}$  (Run 1-124) and  $(5.69 \pm 0.016) \times 10^{-4} \text{ sec.}^{-1}$ .



in ethanol and acetic acid respectively. At 70° with 0.03 M added potassium acetate, the rates for solvolysis of t-butyl chloride in anhydrous ethanol and acetic acid are  $3.19 \times 10^{-5}$  and  $7.12 \times 10^{-5} \text{ sec.}^{-1}$  respectively (Table XXXII, reference 96). Hence, t-butyl chloride should be relatively stable under the conditions of solvolysis of t-butylethylmethylsulfonium salts.

The mechanism proposed by Hyne could account for the formation of t-butyl chloride. It could not however account for the change in the fraction of olefin. Only that portion of the product arising via t-butyl chloride formation would in this mechanism give rise to a fraction of olefin greater than that observed for the solvolysis of the sulfonium salt in the absence of lithium chloride. To account for the results all of the sulfonium salt would have to first form t-butyl chloride and then undergo solvolysis. This is not observed.

An alternative explanation of the results is that the solvolysis of t-butyl sulfonium halides and the corresponding t-butyl halides proceed through the same ionic intermediate "In". We suggest that this intermediate is a t-butyl cation halide ion ion-pair.





This common intermediate would account for the variation in the fraction of olefin and could also account for the formation of t-butyl chloride. Two possibilities exist. Either the anion directly removes the proton from the intermediate or it indirectly assists in the removal of the proton by the solvent. The detection of t-butyl chloride during the solvolysis of t-butylsulfonium chloride is, in this solvent, equivalent to the detection of return from the "intermediate" in the solvolysis of t-butyl chloride. Thus, sulfonium salts may prove to be excellent models for the study of reaction intermediates involved in the solvolysis of alkyl halides.

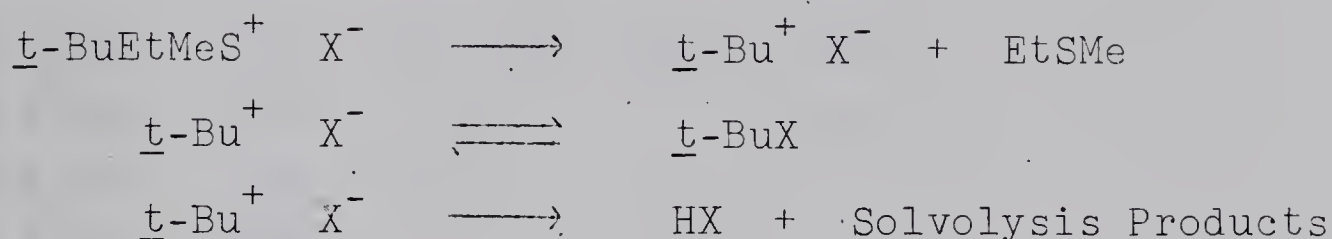
We have seen that the fraction of elimination and substitution are strongly influenced by the anion. Moreover the solvent effects on the product distribution are completely different for halides and perchlorates. Changing from ethanol to the less nucleophilic and less dissociating solvent acetic acid causes a small decrease in the fraction of elimination from t-butylethylmethylsulfonium perchlorate but causes a large increase in the fraction of elimination for the corresponding sulfonium halide similar to the increase in the fraction of elimination for alkyl halides. Addition of acetic anhydride to acetic acid increases the ionizing power but has no effect on the nucleophilicity of the solvent. In 50 volume per cent acetic anhydride-acetic acid, the





fraction of elimination is within experimental error of that in pure acetic acid.

As shown in Table XXVI, the mole per cent of sulfide produced reaches 100 per cent faster than the mole per cent of acid produced. This reflects a reaction step in which sulfide is produced but not acid.



The radiochemical method of measuring the rate of solvolysis of sulfonium salts as developed by Hyne and Wolfgang (93) also measures the rate of formation of sulfide. The authors have equated this to the rate of total solvolysis. It should be pointed out that this is true only when the solvolysis of the t-butyl halide formed is faster than the rate of solvolysis for the t-butylsulfonium salt. Since a finite amount of t-butyl chloride was observed during ethanolysis and acetolysis of t-butylethylmethylsulfonium perchlorate in the presence of added lithium chloride, Tables XXVI and XXVIII, it is clear that the rate of formation of sulfide is not always equivalent to the total rate of solvolysis. Table XXXII illustrates that the rate of solvolysis of t-butyl chloride in 100 per cent ethanol and acetic acid is less than the rate





TABLE XXXII

RATES OF SOLVOLYSIS OF t-BUTYL HALIDES AND SULFONIUM SALTS

Solvent	$10^6 k \text{ (sec.}^{-1}\text{)}$			
	<u>t</u> -BuCl	<u>t</u> -BuBr	<u>t</u> -BuMe <sub>2</sub> SCl	<u>t</u> -BuEtMeS ClO <sub>4</sub>
Temperature 25°				
100% EtOH	0.0860 (48) <sup>a</sup>	5.69 (90)	0.36 <sup>b</sup>	0.857 <sup>c</sup>
90% EtOH	1.71 (9)	372 (90)	0.20 <sup>b</sup>	
80% EtOH	9.14 (9)		0.17 <sup>b</sup>	
60% EtOH	126 (9)			
40% EtOH	1294 (9)			
H <sub>2</sub> O	31200 (76)		0.094 (77)	0.256 <sup>c</sup>
HOAc	0.213 (48)		0.14 <sup>d</sup>	0.657 <sup>c</sup>
Temperature 70°				
EtOH	31.9 (96)		230 <sup>e</sup>	728 ± 50 <sup>c</sup>
HOAc	71.2 (96)		130 <sup>d</sup>	569 ± 16 <sup>c</sup>
H <sub>2</sub> O			116 (77)	289 ± 11 <sup>c</sup>

a) Numbers in bracket indicate references; b) value extrapolated from data of Hyne (17, 19) and Swain (15) and their co-workers; c) this work; d) extrapolated from the value of Swain,  $8.33 \times 10^{-6} \text{ sec.}^{-1}$  at 50.4°, assuming the same activation energy as t-butylethylmethylsulfonium salts; e) perchlorate salt at 69.46°, reference (19).



of solvolysis of the corresponding sulfonium salts.

The effects of varying the anion and varying the solvent on the product distribution for the solvolysis of t-amylethylmethylsulfonium and 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts are similar to that observed for the solvolysis of t-butylethylmethylsulfonium salts. Namely, (i) the fraction of elimination for the solvolysis of the sulfonium halide is greater than for the solvolysis of the corresponding sulfonium perchlorate. (ii) Changing the solvent from ethanol to acetic acid causes a small decrease in the amount of olefin produced in the solvolysis of the sulfonium perchlorate but causes a large decrease in the amount of olefin produced in the solvolysis of the corresponding sulfonium halide. Therefore conclusions reached for the solvolysis of t-butylsulfonium salts also apply to substituted t-butylsulfonium salts.



## EXPERIMENTAL

### REAGENTS AND MATERIALS

#### Isobutene

A small amount of Phillips isobutene was liquified in a Dry-ice trap. A 25 ml. volumetric flask containing 5 ml. of anhydrous solvent, ethanol or acetic acid, was accurately weighed. An aliquot of liquid isobutene was added to the solvent. The flask was quickly stoppered and weighed, then solvent was added to the mark. Accurately known aliquots of this solution was transferred to the control solutions. Solutions containing isobutene was transferred to ampoules which were sealed as quickly as possible.

#### t-Butyl Ethyl Ether, t-Butyl Acetate, 2-Methyl-1-butene, 2-Methyl-2-butene

Gas chromatographic analyses of samples of t-butyl ethyl ether and t-butyl acetate (Eastman Organic Chemicals), 2-methyl-1-butene (K & K Laboratories Inc.) and 2-methyl-2-butene (Matheson Coleman and Bell) indicated only one peak in the chromatograms. These compounds were used without further treatment.





t-Butyl Chloride

Eastman Organic Chemicals t-butyl chloride was purified by gas chromatography at low temperature using an Aerograph Model A 90 3P. A 2 meter Ucon Oil (polypropylene glycol) column was employed under the following conditions: column temperature,  $45^{\circ}$ , pressure, 60 ppsi, helium gas flow, 220 cc/min.

t-Amyl Ethyl Ether

Concentrated sulfuric acid (50 ml.) was added carefully to 500 ml. of distilled water in a two-liter flask equipped with a dropping funnel and condenser. The system was allowed to cool and a 250 ml. quantity of 95 per cent ethanol was added. The temperature was raised to  $70^{\circ}$ , 70 ml. of t-amyl alcohol was added and the flask was heated so that the product distilled slowly. An azeotrope of t-amyl ethyl ether and ethanol boils at  $66.6^{\circ}$  (92). The distillate was washed three times with 10 per cent potassium carbonate, then washed with small portions of water until the ethanol peak in the gas chromatographic analysis of the liquid disappeared. The ether layer was dried over anhydrous potassium carbonate and fractionally distilled through a 40 cm. Vigreux column to separate the ether from the olefinic side products. Yield 60 g. (30 per cent), b.p.



99° at 700 mm.,  $n_D^{25}$  1.3908 (reported (92): 101°,  $n_D^{20}$  1.3912). N.m.r. ( $CDCl_3$ ):  $\tau$  9.14 (t,  $J=7.0$  cps., 3 H), 8.87 (s, 6 H), 8.87 (t,  $J=7.0$  cps., 3 H), 8.51 (q,  $J=7.0$  cps., 2 H), 6.65 (q,  $J=7.0$  cps., 2 H).

#### t-Amyl Acetate

t-Amyl acetate was prepared from 8.8 g. (0.1 mole) of t-amyl alcohol by the procedure described by Vogel (91) for the preparation of tertiary alkyl acetates. Yield 6.9 g. (53 per cent), b.p. 120.0-120.5°,  $n_D^{25}$  1.3973 (reported (91): 62-64° at 97 mm.,  $n_D^{20}$  1.3980). N.m.r. ( $CDCl_3$ ):  $\tau$  9.12 (t,  $J=7.5$  cps., 3 H), 8.60 (s, 6 H), 8.23 (q,  $J=7.5$  cps., 2 H), 8.05 (s, 3 H). Infrared: 1735, 1255, 1232, 1200 and 1013  $cm^{-1}$ .

#### 1-Phenyl-2-methylpropene

K & K Laboratories "isocrotylbenzene",  $n_D^{25}$  1.5346, was purified by gas chromatography using an Aerograph Model A 90 3P. A 2 meter polypropylene glycol column was employed under the following conditions: column temperature, 100°, pressure 60 ppsi., helium gas flow 60 cc/min. The purified 1-phenyl-2-methylpropene had  $n_D^{25}$  1.5383 (reported (94):  $n_D^{25}$  1.5367).

#### 3-Phenyl-2-methylpropene

Aldrich Chemicals "methallylbenzene",  $n_D^{20}$  1.5069,



was purified as described above. 3-Phenyl-2-methylpropene has  $n_D^{25}$  1.5064 (reported (94):  $n_D^{25}$  1.5049).

1-Phenyl-2-methyl-2-propyl Ethyl Ether

A 5.0 g. (0.33 mole) quantity of 1-phenyl-2-methyl-2-propanol (K & K Laboratories "phenyl-tert-butanol") was added to a cooled solution of 10 ml. of concentrated sulfuric acid in 50 ml. of anhydrous ethanol. The solution was stirred at room temperature for several weeks, then diluted with 150 g. of crushed ice and extracted as described for the preparation of 1-methoxy-2-methyl-2-propyl ethyl ether. The crude product (4 g.) was shown by gas chromatography to contain 1-phenyl-2-methylpropene, 3-phenyl-2-methylpropene, 1-phenyl-2-methyl-2-propyl ethyl ether and some starting alcohol, 1-phenyl-2-methyl-2-propanol. The mixture was chromatographed on 300 g. of alumina, activity II. The olefins were eluted in the first 250 ml. cut of pentane, the ether in the third and the alcohol remained on the column. Vacuum distillation gave 0.4 g. (7 per cent) of pure 1-phenyl-2-methyl-2-propyl ethyl ether. B.p.  $93^\circ$  at 18 mm. N.m.r. ( $\text{CDCl}_3$ ):  $\tau$  8.88 (s, 6 H), 8.82 (t,  $J=7.0$  cps., 3 H), 7.22 (s, 2 H), 6.51 (q,  $J=7.0$  cps., 2 H), 2.78 (s, 5 H). Infrared: 3080, 3060, 3020, 1597, 1491, 1065, 720 and 696  $\text{cm}^{-1}$ .

Anal. Calcd. for  $\text{C}_{12}\text{H}_{18}\text{O}$ : C, 80.85; H, 10.18.

Found: C, 80.87, 80.84; H, 10.00, 9.74.





1-Phenyl-2-methyl-2-propyl Acetate

1-Phenyl-2-methyl-2-propyl acetate was prepared from 9.5 g. (0.63 mole) of 1-phenyl-2-methyl-2-propanol (K & K Laboratories "phenyl-tert-butanol") by the procedure described for the preparation of 1-methoxy-2-methyl-2-propyl acetate. The n.m.r. spectrum of the distillate (6.2 g.) showed that it contained approximately 36 per cent acetate, the remainder being starting alcohol. The crude product was chromatographed on 300 g. of alumina, activity II. The acetate was eluted in the second 250 ml. cut of pentane. Vacuum distillation gave 1.0 g. (8 per cent) of pure 1-phenyl-2-methyl-2-propyl acetate, b.p. 117-118° at 18 mm.,  $n_D^{25}$  1.4910 (reported: (95) b.p. 101-105° at 10 mm.,  $n_D^{20}$  1.4980). N.m.r. ( $CDCl_3$ ):  $\tau$  8.57 (s, 6 H), 8.04 (s, 3 H), 6.93 (s, 2 H), 2.77 (s, 5 H). Infrared: 3080, 3055, 3025, 1731, 1596, 1578, 1492, 1247, 1116, 728 and 698  $cm^{-1}$ . Anal. Calcd. for  $C_{12}H_{16}O_2$ : C, 74.97; H, 8.39. Found: C, 75.21, 74.72; H, 8.16, 8.07.

ANALYSES

The product analyses for the solvolysis of 1-phenyl-2-methyl-2-propylethylmethylsulfonium salts were obtained by isolating the products from the solvent and injecting a sample into the gas chromatographic apparatus (Method I).





For the solvolysis of t-butylethylmethylsulfonium and t-amylethylmethylsulfonium salts, the products were not isolated from the solvent, but rather the reaction solution was injected directly into the gas chromatographic apparatus (Method II).

The different columns and conditions of operation employed for gas chromatographic analyses are listed in Table XXXIII. For each determination, the analytical method was calibrated by control analyses on solutions of known composition.

Details of the analysis of the product distribution from the ethanolysis of 1-phenyl-2-methyl-2-propylethylmethylsulfonium perchlorate and the acetolysis of t-butylethylmethylsulfonium perchlorate are presented as typical examples to illustrate Methods I and II respectively.

#### METHOD I

##### Ethanolysis of 1-Phenyl-2-methyl-2-propylethylmethylsulfonium Perchlorate Control Analyses, Run 4-36

Two standard solutions in anhydrous ethanol were prepared. The first, 4-36.1, contained 1-phenyl-2-methyl-2-propyl ethyl ether (0.0156 M), 1-phenyl-2-methylpropene (0.0242 M), 3-phenyl-2-methylpropene (0.0235 M) and ethyl methyl sulfide (0.0311 M). The second, 4-36.2, contained



TABLE XXXIII

## COLUMNS AND CONDITIONS OF OPERATION FOR GAS CHROMATOGRAPHIC ANALYSES

Salt	Solvent	Column (length m.)	Temp. °C.	Press. psi.	Helium flow cc/min	Detect current ma.	Products (retention times in min. are in brackets.)
I	EtOH	F (2)	27	19	170	270	Isobutene(0.8), <u>t</u> BuCl(3.6), <u>t</u> BuOEt (5.4), EtSMe(9), <u>CH</u> <sub>2</sub> Cl <sub>2</sub> , internal standard(16).
I	HOAc	R (5)	89	20	170	250	Isobutene(1.3), <u>t</u> BuCl(2.6), EtSMe (4.2), <u>t</u> -BuOAc(6.8), toluene, in- ternal standard(13).
III	EtOH	F (2)	27	19	170	270	2Me1butene(1.4), 2Me2butene(1.8), <u>t</u> AmOEt(13), <u>CH</u> <sub>2</sub> Cl <sub>2</sub> , internal standard(16).
III	HOAc	R (5)	89	20	170	250	2Me1butene(1.8), 2Me2butene(2.1), <u>t</u> AmOAc(14), EtSMe(4.2), benzene, internal standard(6.8).
IV	EtOH	C (2)	152	21	95	230	3Ø2Mepropene(5.9), 1Ø2Mepropene (7.6), 1Ø2Me2PrOEt(16), naphtha- lene, internal standard(13).
IV	HOAc	P (2)	122	21	120	240	3Ø2Mepropene(2.9), 1Ø2Mepropene (3.5), 1Ø2Me2PrOAc(16), naphtha- lene, internal standard(20).

I t-butylethylmethylsulfonium, III t-amylethylmethylsulfonium, IV 1-phenyl-2-methyl-2-propylethylmethylsulfonium. F Perkin-Elmer column F, tetraethylethyleneglycol-methyl ether. R 20% Ucon oil LB550X, polypropyleneglycol, on Chromosorb W. C Perkin-Elmer column C, silicone oil DC200. P Perkin-Elmer column P, succinate ester of diethyleneglycol.



naphthalene (0.248 M), benzene (0.402 M) and 2,6-lutidine (0.656 M).

A series of control solutions containing various ratios of each component relative to the internal standard, naphthalene, was obtained by transferring accurately known aliquots of samples 4-36.1 and 4-36.2 to 25 ml. volumetric flasks by means of calibrated automatic pipettes. After dilution to the mark with anhydrous ethanol, the solutions were equilibrated by shaking the flask 100 times. The control solutions and the amounts of stock solutions in each are listed in Table XXXIV.

TABLE XXXIV

CONTROL SOLUTIONS FOR THE PRODUCT ANALYSIS OF 1-PHENYL-2-METHYL-2-PROPYLETHYLMETHYLSULFONIUM SALTS IN ANHYDROUS ETHANOL

Controls	Aliquots of Stock Solutions (ml.)	
	4-36.1	4-36.2
4-36.3	1 x 0.942	1.922
4-36.4	2 x 0.942	1.922
4-36.5	3 x 0.942	1.922
4-36.6	1 x 5.015	1.922
4-36.7	2 x 5.015	1.922
4-36.8	4 x 5.015	1.922





The weights of each component in the control solutions and their concentration in moles per liter are listed in Table XXXV. Aliquots of each control solution were transferred to ampoules which were sealed immediately. The ampoules were placed in the 70.00° constant temperature bath for 3.5 hours. This corresponds to 17 half-lives of solvolysis. The ampoules were removed and equilibrated to 25.00°.

A 4.947 ml. aliquot was transferred to a 60 ml. separatory funnel containing 25 ml. of boiled distilled water and 25 ml. of a 1 : 1 pentane-ethyl ether mixture. The separatory funnel was shaken exactly 45 times, the pressure being released at every count of 15. The aqueous layer was drained and discarded. The extraction was repeated with 25 ml. of 2 per cent sulfuric acid and twice more with 25 ml. portion of boiled distilled water, discarding the aqueous layer each time. The pentane-ethyl ether solution was transferred to a 50 ml. Erlenmeyer flask containing 5 g. of anhydrous potassium carbonate. The flask was swirled for one minute and allowed to stand for 5 minutes before the mixture was filtered through glass wool into a 50 ml. pear-shaped flask. The potassium carbonate was washed with 5 ml. of pentane-ethyl ether and the washings were filtered into the pear-shaped flask. The solvent was removed by careful distillation through



TABLE XXXV

CONTROL ANALYSES OF THE PRODUCTS OF ETHANOLYSIS OF 1-PHENYL-2-METHYL-2-PROPYLETHYLMETHYLSULFONIUM SALTS. RUN 4-36.

Column and conditions: see Table XXXIII. Internal standard: naphthalene.

Sample <sup>a</sup>	Components	Weight g./25ml.	Conc. M.	Rel. areas	Calculated weight g./25ml.
4-36.3	3- $\phi$ -2-Me-propene	0.00292	0.000888	0.043	0.0026
	1- $\phi$ -2-Me-propene	0.00301	0.000911	0.043	0.0026
	naphthalene	0.0611	0.0191	1	
	1- $\phi$ -2-Me-2-Pr-OEt	0.00262	0.000587	0.040	0.0025
	Et-S-Me	0.00223	0.00117		
4-36.4	3- $\phi$ -2-Me-propene	0.00584	0.0177	0.092	0.0056
	1- $\phi$ -2-Me-propene	0.00602	0.00182	0.104	0.0064
	naphthalene	0.0611	0.0191	1	
	1- $\phi$ -3-Me-2-Pr-OEt	0.00523	0.00117	0.069	0.0042
	Et-S-Me	0.00446	0.0234		
4-36.5	3- $\phi$ -Me-propene	0.00877	0.00265	0.110	0.0068
	1- $\phi$ -2-Me-propene	0.00903	0.00273	0.128	0.0080
	naphthalene	0.0611	0.0191	1	
	1- $\phi$ -2-Me-2-Pr-OEt	0.00785	0.00176	0.095	0.0080
	Et-S-Me	0.00669	0.00351		
4-36.6	3- $\phi$ -2-Me-propene	0.0156	0.00471	0.241	0.0147
	1- $\phi$ -2-Me-propene	0.0160	0.00485	0.254	0.0155
	naphthalene	0.0611	0.0191	1	
	1- $\phi$ -2-Me-2-Pr-OEt	0.0139	0.00312	0.197	0.0121
	Et-S-Me	0.0119	0.00625		

Continued....



TABLE XXXV Continued.

Sample <sup>a</sup>	Components	Weight g./25ml.	Conc. M.	Rel. areas	Calculated weight g./25ml.
4-36.7	3- $\phi$ -2-Me-propene	0.0311	0.00941	0.511	0.0312
	1- $\phi$ -2-Me-propene	0.0321	0.00970	0.532	0.0325
	naphthalene	0.0611	0.0191	1	
	1- $\phi$ -2-Me-2-Pr OEt	0.0279	0.00625	0.393	0.0240
	Et-S-Me	0.0238	0.0123		
4-36.8	3- $\phi$ -2-Me-prpene	0.0622	0.0188	0.973	0.0591
	1- $\phi$ -2-Me-propene	0.0641	0.0194	1.05	0.0639
	naphthalene	0.0611	0.0191	1	
	1- $\phi$ -2-Me-2-Pr OEt	0.0557	0.0125	0.762	0.0465
	Et-S-Me	0.0476	0.0246		

a) All samples contain 0.0191 M naphthalene, 0.0504 M 2,6-lutidine and 0.0309 M benzene.





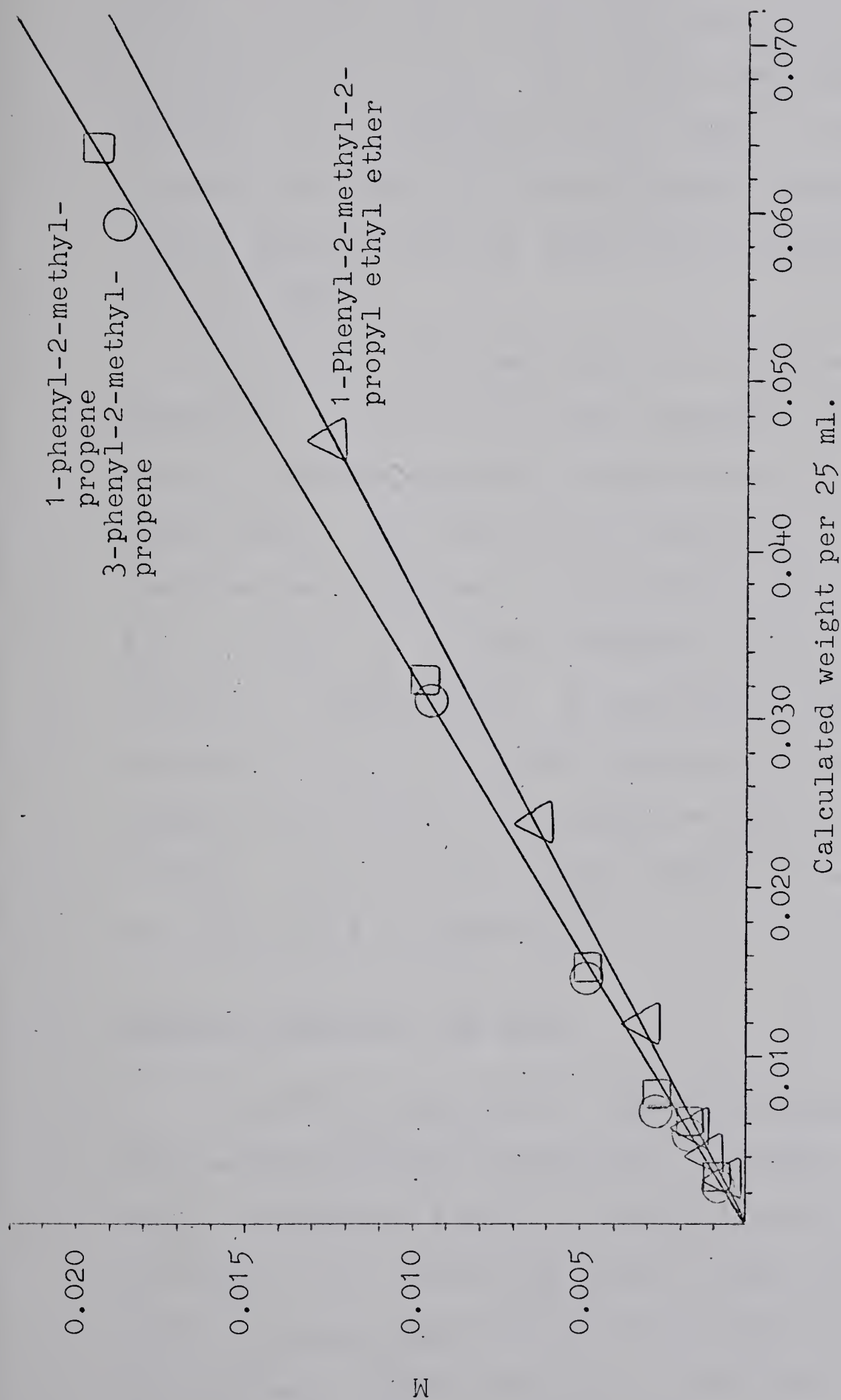


Figure XII. Calibration curve for the product analysis of 1-phenyl-2-methyl-2-propyl-ethylmethylsulfonium salts with added 2,6-lutidine in anhydrous ethanol using naphthalene as internal standard. Run 4-36.





a 30 cm. Vigreux column. The column was rinsed by adding 5 ml. of ethyl ether through the top. The ether was distilled very slowly. The residue was dissolved by adding 1 ml. of anhydrous ethyl ether. A 50  $\mu$ l sample was injected into the gas chromatographic apparatus. The column employed and the conditions of operation are listed in Table XXXII.

Peak areas were measured with a Honeywell Disc Chart Integrator. The area of each component relative to the area of internal standard, naphthalene, is listed in Table XXXIV. The "Calculated weight per 25 ml." of each component was obtained by multiplying its relative area by the weight of internal standard per 25 ml. of solution (0.0611 g. naphthalene). A calibration curve was constructed by plotting the calculated weight of each component per 25 ml. of solution vs their known concentration. In all cases a good straight line was obtained as illustrated in Figure XII.

#### Product Analyses. Run 4-40

A 0.2401 g. quantity of 1-phenyl-2-methyl-2-propyl-ethylmethylsulfonium perchlorate was added to a tared 50 ml. volumetric flask. A known aliquot (2 x 1.922 ml.) of sample 4-36.2 described above (0.248 M naphthalene, 0.402 M benzene and 0.656 M 2,6-lutidine) was also added to the flask. After dilution to the mark with anhydrous



ethanol and mixing by shaking the flask 100 times, aliquots were transferred to ampoules which were sealed and treated in exactly the same manner as the control runs. The isolation and analysis was also conducted in exactly the same way as the control runs. The "Calculated weight of each component per 25 ml. of solution", was obtained by multiplying the peak area relative to the internal standard naphthalene, by the known weight of internal standard per 25 ml. of solution (0.0611 g.). The concentration of each component was obtained from the "calculated weight per 25 ml." by interpolation on the standardization curve (Figure XII). The results are presented in Table XXXV. The mole per cent of each component was calculated by dividing the concentration of each component by the initial concentration of 1-phenyl-2-methyl-2-propylethylmethylsulfonium perchlorate (0.01555 M) and multiplying by 100.

The amount of ethyl methyl sulfide produced was analyzed by injecting a 50  $\mu$ l aliquot of the reaction solution into the gas chromatographic apparatus. An analogous procedure is described in detail in Method II. The added benzene served as the internal standard. A 2 meter Perkin-Elmer column K (polyethylene glycol) was employed under the following conditions: power setting, 40; temperature, 32; pressure, 21 ppsi; helium gas flow, 95 cc./min.; detector current, 270 ma.; chart speed, 0.25



in./min.. The standardization curve is illustrated in Figure XIII and the results of the analysis are presented in Table XXXV.

Two aliquots were titrated with a standard solution of sodium methoxide in methanol using phenolphthalein as indicator. The concentration of the acid produced was  $0.01539 \pm 0.00007$  molar; this corresponds to  $99 \pm 1$  per cent of the theoretical amount.

#### Analysis of Acetolysis Products

For runs conducted in acetic acid, the procedure was modified as follows: (i) sodium acetate was the base added to neutralize the acid formed during solvolysis. (ii) In the isolation procedure, the pentane-ethyl ether solution was washed twice with water, once with 5% sodium bicarbonate solution and once again with water. (iii) The gas chromatographic column employed and the conditions of operation are listed in Table XXXIII.

#### METHOD II

##### Acetolysis of t-Butylethylmethylsulfonium Perchlorate

##### Control Analyses, Run 3-258

A series of control solutions containing various ratios of isobutene, ethyl methyl sulfide and t-butyl





TABLE XXXVI

PRODUCT ANALYSES OF 1-PHENYL-2-METHYL-2-PROPYLETHYLMETHYL-SULFONIUM PERCHLORATE (0.01555 M) WITH ADDED 2,6-LUTIDINE (0.0504 M) IN ANHYDROUS ETHANOL AT 70.00°. RUN 4-40.

Column and conditions: see Table XXXIII. Internal standard: naphthalene.

Sample	Components	Rel. areas	Calculated weight g./25ml.	Conc. M.	mole %
4-40.1	3- $\phi$ -2-Me-propene	0.145	0.0089	0.0027	17
	1- $\phi$ -2-Me-propene	0.182	0.0111	0.0034	22
	naphthalene	1			
	1- $\phi$ -2-Me-2-Pr OEt	0.591	0.0360	0.0096	62
4-40.1	3- $\phi$ -2-Me-propene	0.136	0.0083	0.0026	17
	1- $\phi$ -2-Me-propene	0.168	0.0103	0.0032	21
	naphthalene	1			
	1- $\phi$ -2-Me-2-Pr OEt	0.606	0.370	0.0032	64
4-40.2	3- $\phi$ -2-Me-propene	0.129	0.0079	0.0024	15
	1- $\phi$ -2-Me-propene	0.167	0.0102	0.0031	20
	naphthalene	1			
	1- $\phi$ -2-Me-2-Pr OEt	0.606	0.0370	0.0099	64
4-40.2	3- $\phi$ -2-Me-propene	0.133	0.0081	0.0025	16
	1- $\phi$ -2-Me-propene	0.168	0.0102	0.0031	20
	naphthalene	1			
	1- $\phi$ -2-Me-2-Pr OEt	0.605	0.0370	0.0099	64

Continued....



TABLE XXXVI Continued.

Sample	Components	Rel. areas	Calculated weight g./25ml.	Conc. M.	Mole %
4-40.3 <sup>a</sup>	Ethyl methyl sulfide	0.475	0.0277	0.0155	100
	Benzene	1			
	H <sup>+</sup>			0.01545 <sup>b</sup>	99
4-40.3 <sup>a</sup>	Ethyl methyl sulfide	0.471	0.0284	0.0153	98
	Benzene	1			
	H <sup>+</sup>			0.01532 <sup>b</sup>	99

a) Analyses by Method II; b) obtained by titration.



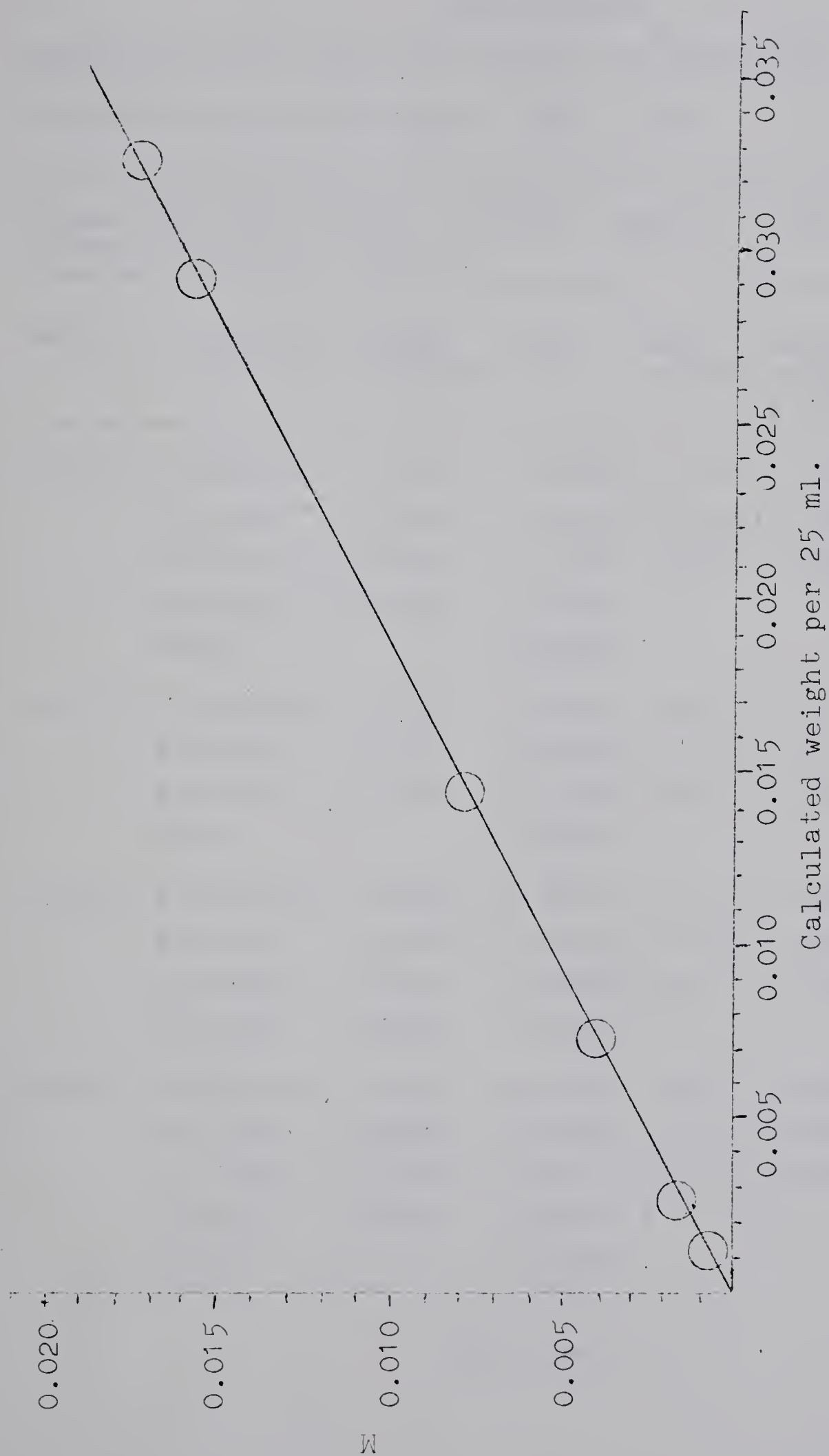


Figure XIII. Calibration curve for analysis for ethyl methyl sulfide using benzene as internal standard. Run 3-260.



TABLE XXXVII

CONTROL ANALYSES FOR THE PRODUCTS OF ACETOLYSIS OF t-BUTYL-ETHYLMETHYLSULFONIUM SALTS. RUN 3-258.

Column and conditions: see Table XXXIII. Internal standard: toluene (0.0469 g./25ml.).

Sample	Components	Weight g./25ml.	Conc. M.	Rel. areas	Calcd. weight g./25ml.	Rel. <sup>a</sup> areas	Calcd. weight g./25ml.
3-258.7	Isobutene	0.00263	0.00188	0.039	0.0018	0.050	0.0023
	Et-S-Me	0.00301	0.00158	0.069	0.0032	0.053	0.0025
	<u>t</u> -Bu-OAc	0.0429	0.0148	0.802	0.0376	0.788	0.0369
	Toluene	0.0469	0.0204	1		1	
	NaOAc		0.02875				
3-258.8	Isobutene	0.0132	0.00941	0.242	0.0113	0.290	0.0136
	Et-S-Me	0.0151	0.00792	0.187	0.0135	0.308	0.0144
	<u>t</u> -Bu-OAc	0.0215	0.00739	0.413	0.0194	0.392	0.0184
	NaOAc		0.02875				
3-258.9	Isobutene	0.00660	0.00470	0.141	0.0066	0.137	0.0064
	Et-S-Me	0.00754	0.00396	0.158	0.0074	0.157	0.0074
	<u>t</u> -Bu-OAc	0.0107	0.00369	0.211	0.0099	0.210	0.0098
	Toluene	0.0469	0.0204	1		1	
3-258.10	Isobutene	0.0264	0.0188	0.554	0.0266	0.560	0.0262
	Et-S-Me	0.0302	0.0158	0.611	0.0286	0.612	0.0287
	<u>t</u> -Bu-OAc	0.00428	0.00147	0.081	0.0038	0.10	0.0048
	Toluene	0.0469	0.0204	1		1	
	NaOAc		0.02875				

Continued....





TABLE XXXVII Continued.

Sample	Components	Weight g./25ml.	Conc. M.	Rel. areas	Calcd. weight g./25ml.
3-258.11	Isobutene	0.00132	0.000937	0.026	0.0012
	Et-S-Me	0.00150	0.000789	0.032	0.0015
	<u>t</u> -Bu-OAc	0.00214	0.000737	0.040	0.0019
	Toluene	0.00214	0.0204	1	
	NaOAc		0.02875		

a) Duplicate analyses.



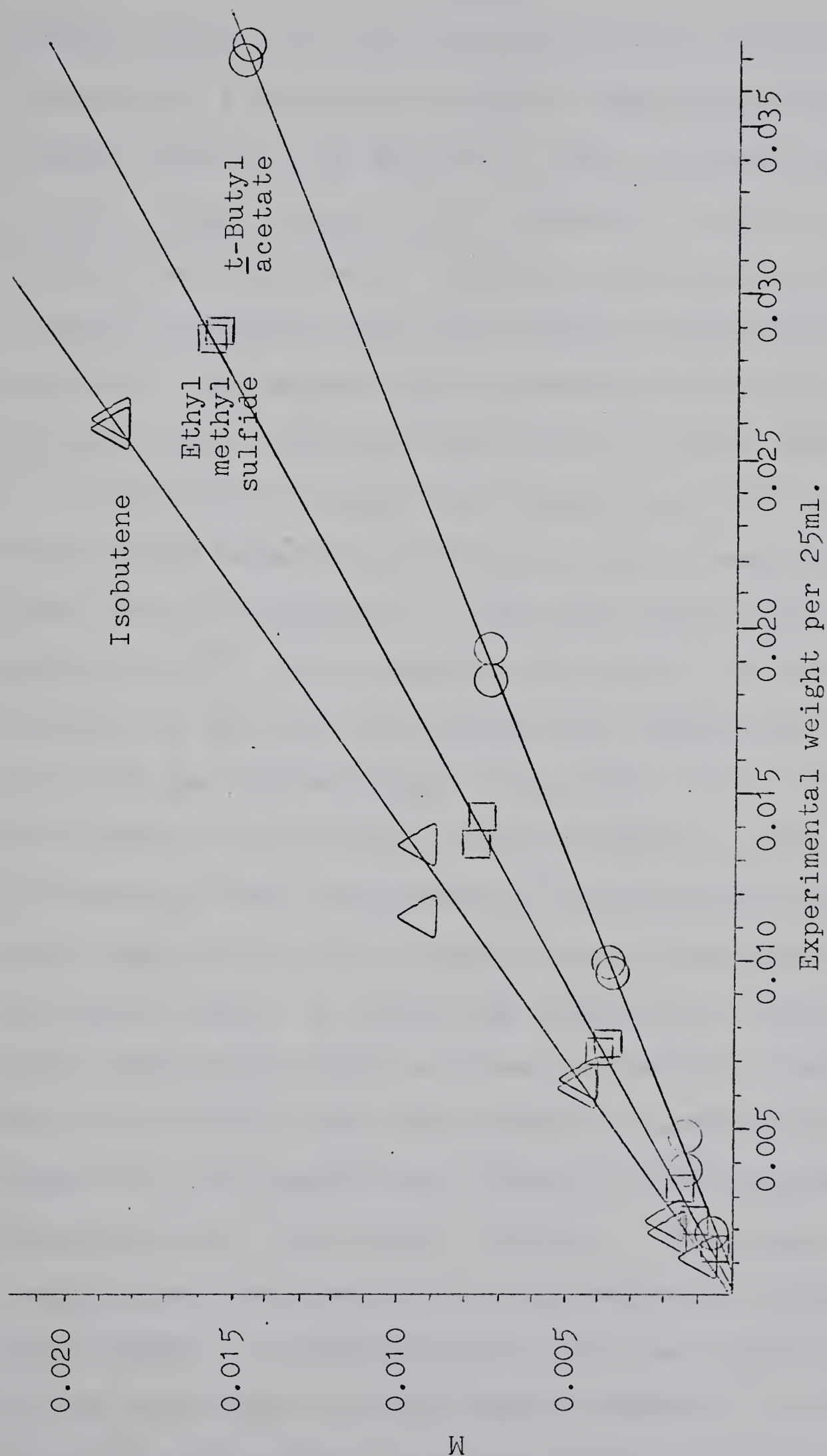


Figure XIV. Calibration curve for the product analysis of t-butylethylmethylsulfonium salts with added sodium acetate in anhydrous acetic acid using toluene as internal standard. Run 3-258.



acetate relative to the internal standard, toluene, were prepared by a procedure similar to the preparation of control solutions in Method I. Each solution also contained a known aliquot of the standard sodium acetate solution as added base. Control solutions were transferred to ampoules which were sealed as quickly as possible. The weight and concentration of each component in the control solutions are listed in Table XXXVI.

The sealed ampoules were placed in a 70° constant temperature bath for 5.75 hours; this corresponds to 17 half-lives of solvolysis. They were removed and equilibrated to 10°. Upon opening the ampoules, a 50  $\mu$ l aliquot of the reaction solution was immediately injected into the gas chromatographic apparatus. Since the amount of solvent is much larger than the amounts of the products, the detector must be operated at high sensitivity. In this range, the solvent peak on the chromatogram is extremely large. A column and conditions of operation (low temperature) must be chosen so that all components are eluted faster than the solvent, otherwise their peaks will be blanked out. Total per cent recovery is ascertained by the internal standard. The column employed and the conditions of operation are listed in Table XXXIII. A standardization curve was constructed in the same manner as described in Method I. In all cases, a good straight line was obtained when the





"Calculated weight of each component per 25 ml. of solution" was plotted vs its known concentration. For example, Figure XIV illustrates the calibration curve for Run 3-258.

Product Analyses, Run 3-264

An accurately known aliquot of standard sodium acetate solution, prepared as described in Chapter I, was added to accurately known amounts of t-butylethylmethylsulfonium perchlorate and toluene in a tared volumetric flask. After dilution to the mark with anhydrous acetic acid, and thorough mixing, aliquots were transferred to ampoules which were sealed, placed in the 70° constant temperature bath for 5.75 hours and analyzed in exactly the same way as the control runs. The results are presented in Table XXXVII. As in Method I, the concentration of each component was obtained from its calculated weight per 25 ml. of solution by interpolation on the standardization curve (Figure XIV). The mole per cent product distribution was calculated by dividing the concentration of each component by the initial concentration of t-butylethylmethylsulfonium perchlorate (0.01400 M) and multiplying by 100.

Three aliquots of the reaction solution were titrated with a standard perchloric acid solution in glacial acetic acid using p-naphtholbenzein as indicator.



The acid produced during solvolysis was  $0.001366 \pm 0.001$  molar. This corresponds to  $98 \pm 1$  per cent of the theoretical amount of acid.

#### Analysis of Ethanolysis Products

For analyses on products in ethanol a similar procedure was used with the following modifications: (i) 2,6-lutidine was the base added to neutralize the acid formed during solvolysis; (ii) a different column and internal standard (refer to Table XXXIII) were employed.

#### Product Analyses for the Solvolysis of t-Amylethylmethylsulfonium Salts

The analyses of the product distribution from the solvolysis of t-amylethylmethylsulfonium salts was conducted by a procedure similar to that as described for the analysis of t-butylethylmethylsulfonium salts, Method II, except that the ampoules were placed in a  $50^{\circ}$  constant temperature bath for 16 hours (acetolysis) and 9 hours (ethanolysis). This corresponds to 16 half-lives and 13 half-lives respectively.



TABLE XXXVIII

PRODUCT ANALYSES OF t-BUTYLETHYLMETHYLSULFONIUM PERCHLORATE  
(0.01400 M) WITH ADDED SODIUM ACETATE (0.03052 M) IN  
ANHYDROUS ACETIC ACID AT 70.00°. RUN 3-264.

Column and conditions: see Table XXXIII. Internal standard:  
toluene (0.271 g./25ml.).

Sample	Components	Rel. areas	Calcd. weight g./25ml.	Conc. M.	Mole %
3-264.2	Isobutene	0.0085	0.0023	0.0017	12
	Ethyl methyl sulfide	0.0963	0.0261	0.0144	103
	<u>t</u> -Butyl acetate	0.113	0.0307	0.0121	86
	Toluene	1			
	H <sup>+</sup>			0.1353 <sup>a</sup>	
3-264.2	Isobutene	0.0076	0.0021	0.0016	11
	Ethyl methyl sulfide	0.0893	0.0242	0.0133	95
	<u>t</u> -Butyl acetate	0.116	0.0313	0.0123	88
	Toluene	1			
	H <sup>+</sup>			0.1377 <sup>a</sup>	
3-264.2	Isobutene	0.0091	0.0025	0.0018	13
	Ethyl methyl sulfide	0.0892	0.0241	0.0018	95
	<u>t</u> -Butyl acetate	0.114	0.0308	0.0122	87
	Toluene	1			
	H <sup>+</sup>			0.01369 <sup>a</sup>	

a) Obtained by titration.





BIBLIOGRAPHY

- (1) C. K. Ingold: Structure and Mechanism in Organic Chemistry, Chap. VII. Cornell University Press, Ithaca, New York (1953).
- (2) K. A. Cooper, E. D. Hughes, C. K. Ingold and B. J. McNulty: J. Chem. Soc. 1948, 2038.
- (3) L. P. Hammett: Physical Organic Chemistry, McGraw-Hill Book Company, Inc., New York (1940).
- (4) a) A. Streitwieser Jr.: Chem. Rev. 56, 571 (1956).  
b) A. Streitwieser Jr.: Solvolytic Displacement Reactions, McGraw-Hill Book Company, Inc., New York (1962).
- (5) C. A. Bunton: Nucleophilic Substitution at Saturated Carbon Atom, Elsevier Publishing Company, New York (1963).
- (6) J. Hine: Physical Organic Chemistry, Second Edition. McGraw-Hill Book Company, Inc., New York (1962).
- (7) E. R. Thornton: Solvolysis Mechanisms, The Ronald Press Company, New York (1964).
- (8) E. D. Hughes and C. K. Ingold: J. Chem. Soc. 1933, 1571.
- (9) K. A. Cooper, M. L. Dhar, E. D. Hughes, C. K. Ingold, B. J. McNulty and L. I. Woolf: J. Chem. Soc. 1948, 2043.





- (10) K. A. Cooper, E. D. Hughes, C. K. Ingold, G. A. Maw and B. J. McNulty: J. Chem. Soc. 1948, 2049.
- (11) E. D. Hughes, C. K. Ingold and L. I. Woolf: J. Chem. Soc. 1948, 2084.
- (12) E. D. Hughes and C. K. Ingold: J. Chem. Soc. 1935, 244.
- (13) W. H. Saunders Jr. and S. Asperger: J. Am. Chem. Soc. 79, 1612 (1957).
- (14) W. H. Saunders Jr. and S. E. Zimmerman: J. Am. Chem. Soc. 86, 3789 (1964).
- (15) C. G. Swain, L. E. Kaiser and T. C. E. Knee: J. Am. Chem. Soc. 80, 4089 (1958).
- (16) A. L. Jacobson and J. B. Hyne: J. Am. Chem. Soc. 80, 2418 (1960).
- (17) J. B. Hyne: Can. J. Chem. 39, 1207 (1961).
- (18) J. B. Hyne and J. W. Abrell: Can. J. Chem. 39, 1657 (1961).
- (19) J. B. Hyne and J. H. Jensen: Can. J. Chem. 40, 1394 (1962).
- (20) J. B. Hyne and J. H. Jensen: Can. J. Chem. 41, 1679 (1963).
- (21) J. B. Hyne and H. S. Golinkin: Can. J. Chem. 41, 3139 (1963).
- (22) J. B. Hyne and J. H. Jensen: Can. J. Chem. 43, 57 (1965).
- (23) M. Cocivera and S. Winstein: J. Am. Chem. Soc. 85, 1702 (1963).
- (24) S. Winstein and G. Robinson: J. Am. Chem. Soc. 80, 169 (1958).



- (25) S. Winstein, J. Gall, M. Hoyo and S. Smith: J. Am. Chem. Soc. 82, 1010 (1960).
- (26) S. Winstein, M. Hoyo and S. Smith: Tetrahedron Letters No. 22, 12, 1960.
- (27) D. Darwish and R. A. McLaren: Abstract of Papers Presented Before the Division of Organic Chemistry at the 148th Meeting of the American Chemical Society, Chicago, Illinois, September 1964, p. 44-S.
- (28) R. A. McLaren: Ph. D. Thesis, Alberta, 1964.
- (29) H. L. Goering and E. F. Silversmith: J. Am. Chem. Soc. 77, 6249 (1955).
- (30) H. L. Goering: Rec. of Chem. Prog. 21, 125 (1960).
- (31) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon and K. Mislow: J. Am. Chem. Soc. 88, 3138 (1966).
- (32) M. F. Manning: J. Chem. Phys. 3, 136 (1935).
- (33) J. F. Kincaid and F. C. Henriques Jr.: J. Am. Chem. Soc. 62, 1474 (1940).
- (34) R. E. Weston Jr.: J. Am. Chem. Soc. 76, 2045 (1954).
- (35) F. T. Wall and G. Glocker: J. Chem. Phys. 5, 314 (1937).
- (36) C. C. Costain and G. B. B. M. Sutherland: J. Phys. Chem. 56, 321 (1952).
- (37) W. J. Pope and S. J. Peachey: J. Chem. Soc. 1900, 1072.
- (38) S. Smiles: J. Chem. Soc. 1900, 1174.
- (39) F. G. Holliman and F. G. Mann: J. Chem. Soc. 1930, 2554.
- (40) M. P. Balfe, J. Kenyon and H. Phillips: J. Chem. Soc. 1930, 2554.



- (41) V. N. Ipatieff and H. Pines: J. Am. Chem. Soc. 60, 2731 (1938).
- (42) F. Arndt and P. Nachtmey: Chem. Ber. 59, 448 (1926).
- (43) J. G. Pritchard and F. A. Long: J. Am. Chem. Soc. 78, 6008 (1956).
- (44) a) I. M. Kolthoff: Experientia, Supp. No. 5, 33 (1956).  
b) I. M. Kolthoff and S. Bruckenstein: J. Am. Chem. Soc. 78, 1 (1956).
- (45) W. L. Petty and P. L. Nichols Jr.: J. Am. Chem. Soc. 76, 4386 (1954).
- (46) D. W. Turner: Advances in Physical Organic Chemistry, Edited by V. Gold, Vol 4, 65. Academic Press, Inc., New York (1966).
- (47) R. W. Kiser: Introduction to Mass Spectrometry and Its Applications, Appendix. Prentice-Hall, Inc., Englewood Cliffs, N. J. (1965).
- (48) A. H. Fainberg and S. Winstein: J. Am. Chem. Soc. 78, 2770 (1956).
- (49) Handbook of Chemistry and Physics, 46th Edition, R. C. Weast, Editor in Chief, p. E-50, F-35. The Chemical Rubber Co., Cleveland, Ohio (1965-1966).
- (50) A. A. Frost and R. G. Pearson: Kinetics and Mechanism, p. 98-100 John Wiley and Sons, Inc., New York (1953).
- (51) L. F. Fieser: Experiments in Organic Chemistry, 3rd Edition, p.236. D. Heath and Co., Boston (1957).





- (52) a) American Chemical Society: Specifications 1960: Reagent Chemicals, p.17. Applied Publications, American Chemical Society, Washington, D. C. (1961).  
b) J. Mitchell Jr. and D. M. Smith: Aquametry, Chap. V. Interscience Publishers, Inc., New York (1948).
- (53) S. G. Smith, A. H. Fainberg and S. Winstein: J. Am. Chem. Soc. 83, 624 (1961).
- (54) L. F. Fieser: Experiments in Organic Chemistry, 3rd Edition p. 291. D. Heath and Co., Boston (1957).
- (55) H. C. Brown, S. Johnson and H. Podell: J. Am. Chem. Soc. 76, 5556 (1954).
- (56) S. Winstein and R. Adams: J. Am. Chem. Soc. 70, 840 (1948).
- (57) I. M. Kolthoff and E. B. Sandell: Textbook of Quantitative Inorganic Analysis, 3rd Edition, p. 522. The MacMillan Co., New York (1952).
- (58) S. Winstein, E. Grunwald and L. L. Ingraham: J. Am. Chem. Soc. 70, 826 (1948).
- (59) D. T. McAllan, T. V. Cullen, R. A. Dean and F. A. Fidler: J. Am. Chem. Soc. 73, 3627 (1951).
- (60) A. I. Vogel and D. M. Cowan: J. Chem. Soc. 1943, 16.
- (61) C. L. Butler and L. H. Cretcher: J. Am. Chem. Soc. 55, 2605 (1933).
- (62) F. Zetzche and M. Hubacher: Helv. Chim. Acta. 9, 293 (1926).
- (63) W. E. McEwen, D. M. Coyne and C. A. Vanderwerf: J. Am. Chem. Soc. 78, 3061 (1956).



- (64) C. L. Stevens and B. T. Gillis: J. Am. Chem. Soc. 79, 3448 (1957).
- (65) G. S. Koepl, D. S. Sagatys, G. S. Krishnamurthy and S. I. Miller: J. Am. Chem. Soc. 89, 3396 (1967).
- (66) H. C. Brown: Science, 103, 385 (1946).
- (67) A. T. Bottini and J. D. Roberts: J. Am. Chem. Soc. 80, 5203 (1958).
- (68) A. T. Bottini and J. D. Roberts: J. Am. Chem. Soc. 82, 3599 (1960).
- (69) T. J. Bardos, C. Szantay and C. K. Navada: J. Am. Chem. Soc. 87, 5796 (1965).
- (70) A. B. Turner, H. W. Heine, J. Irving and J. B. Bush Jr.: J. Am. Chem. Soc. 87, 1050 (1965).
- (71) V. F. Brystrov, R. G. Kostyanovski, O. A. Panshin, A. U. Stepanyanto and O. A. Iuzhakova: Opt. Spectry (U. S. S. R.) 19, 122 (1965).
- (72) F. A. L. Anet and J. M. Osyany: J. Am. Chem. Soc. 89, 122 (1965).
- (73) H. A. Bent: Chemical Reviews 61, 275 (1961).
- (74) F. A. L. Anet, R. O. Terpka and D. J. Cram: J. Am. Chem. Soc. 89, 357 (1967).
- (75) R. W. Taft Jr.: "Separation of Polar, Steric and Resonance Effects in Reactions," Chap. 13 in M. Newman's Steric Effects in Organic Chemistry, J. Wiley and Sons, Inc., New York (1956).



- (76) E. A. Moelwyn-Hughes, R. E. Robertson and S. Sugamori:  
J. Chem. Soc. 1965, 1965.
- (77) K. T. Leffler, R. E. Robertson and S. Sugamori: J.  
Am. Chem. Soc. 87, 2098 (1965).
- (78) M. M. Kreevoy and R. W. Taft Jr.: J. Am. Chem. Soc.  
77, 5590 (1955).
- (79) E. D. Hughes: J. Chem. Soc. 1935, 255.
- (80) E. D. Hughes and B. J. McNulty: J. Chem. Soc. 1937, 1283.
- (81) M. M. Tessler and C. A. Vanderwerf: J. Org. Chem.  
30, 405 (1965).
- (82) A. Landis and C. A. Vanderwerf: J. Am. Chem. Soc.  
84, 1606 (1962).
- (83) E. L. Eliel: Stereochemistry of Carbon Compounds,  
p. 236. McGraw-Hill Book Company, Inc., New York (1962).
- (84) D. Darwish and G. Tourigny: Abstract of Papers  
Presented Before the Division of Organic Chemistry  
at the 152nd Meeting of the American Chemical Society,  
New York, N.Y., Sept. 1966, p. 5037.
- (85) D. Darwish and G. Tourigny: J. Am. Chem. Soc. 88,  
4303 (1966).
- (86) R. Scartazzini and K. Mislow: Tetrahedron Letters,  
No. 28, 2719 (1967).
- (87) P. von R. Schleyer and R. D. Nicholas: J. Am. Chem.  
Soc. 83, 4303 (1961).
- (88) P. Z. Bedoukian: J. Am. Chem. Soc. 66, 1325 (1944).



- (89) A. I. Vogel: Practical Organic Chemistry, 3rd Edition, p. 973. John Wiley and Sons, Inc., New York (1956).
- (90) E. D. Hughes, C. K. Ingold, S. Masterman and B. J. MacNulty: J. Chem. Soc. 1940, 899.
- (91) A. I. Vogel: Practical Organic Chemistry, 3rd Edition, p. 384. John Wiley and Sons, Inc., New York (1956).
- (92) T. W. Evans, K. R. Edlund: Ind. Eng. Chem. 28, 1186 (1936).
- (93) J. B. Hyne and R. Wolfgang: J. Phys. Chem. 64, 699 (1960).
- (94) J. F. Bunnett, G. T. Davis and H. Tanida: J. Am. Chem. Soc. 84, 1607 (1962).
- (95) R. Criege, P. Dimroth and R. Schempf: Chem. Ber. 90, 1337 (1957).
- (96) E. Grunwald and S. Winstein: J. Am. Chem. Soc. 70, 846 (1958).







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